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WOOL INTERACTION WITH OXALYL CHLORIDE

BY
IFRIM SAVEL

La présence d'un grand nombre des groupes fonctionnels réactifs liés aux restes latéraux des chaïnes polypeptidiques de la structure de la kératine, détermine pour la fibre de laine une notable réactivité.

Ces groupes fonctionnels réagissent avec plusieurs produits, qui parfois, déterminent la réticulation de la kératine. Au processus de réticulation peuvent participer les groupes hydroxyliques, thioliques, aminiques, carboxyliques etc.

Par traitement de la laine avec du chlorure d'oxalyle, produit très réactif, peuvent réagir, au minimum, les mêmes fonctions chimiques. De cette manière on introduit dans la structure chimique de la kératine des groupes α-dicétoniques, dont la présence est mise en évidence à l'aide de l'aniline, phénylhydrazine et *ortho*-phenylènediamine.

Par la détermination des indices physico-mécaniques, c'est-à-dire la résistance de rupture, l'allongement et le diamètre de la fibre, on a mis en évidence l'apparition des nouvelles liaisons transversales dans la kératine.

1. Introduction. The chemical structure of wool keratin is very complex, being determined both of the great number of different amino acids, chained in the polypeptidic macromolecules and of the spatial orientation of these macromolecules.

The polypeptidic chains contain many functional groups, bound by the side rests of chained amino acids. In the opinion of H o w i t [1] these organic groups may be classified in the following three categories: acid groups, basic groups and another groups. In a relative recent article [2], we have proposed a more complete classification of these groups, classification which reflects much more exact the reality.

The presence of these organic functions, many having polar and reactive character, determines a raised reactivity for the whole wool fibre. In the same time the side rests of the polypeptidic chaines determine a certain steric effect, which minders a more compact packing of the keratinic macromolecules . This steric hindrance and this relative breaked up packing is negatively reflected in the fibre resistance; consequently this constitutes an insufficiency.

The chemical wool keratin structure suggests us many possibilities for its modification, which can improve the fibre properties. These modifications have begun in 1888 year [3] and they are continued nowadays too.

The wool fibre physico-mechanical properties improvement is carried out by the keratin reticulation.

The new cross-linkings determine the wool solubility diminution in urea-bisulphite [5] and in caprolactum-bisulphite [6] reactives, with the condition that these new

cross-linkings to be resistant at the bisulphite reduction action. In the same time, by reticulation the wool behaviour at heatis stabilized and the swelling fibre possibility is also diminished [7].

The present paper has in view the introduction of new cross-linkings, which have carbonyl groups. On this purpose it is used a very reactive substance – the oxalyl chloride.

2. Theoretic Part. New cross-linkings in wool keratin may appear both by the cystinic bond modification, without external substances retention and by wool treatment with inorganic or organic substances, when it participates to the formation of the new cross-linkings also the used external substances.

The cystinic bond transformation in new cross-linkings takes place by treating wool in an alkaline medium [8], when besides the lanthyonine formation, may be formed also another cross-linkings, as the lysino-alanine bond. These new cross-linkings appear also in another conditions [9], [10].

In the new cross-linkings structure may be retained mercury [11], chrome or aluminium atoms [12]. At these new cross-linkings formation are implicated the thyolic and carboxylic groups, which are found in the side rests composition, bound by the polypeptidic chains.

The organic substances are very much used for the wool keratin reticulation; such substances are numerous. On this purpose were used dihalides, which react with thiolic, amino or even with carboxylic groups [13]. With much success was used dihalides, having aromatic nuclei in their structure, with halogen atoms in benzilic position, for instance 4,6-bis-(chlormethyl)-metaxylene; at the reticulation reaction with this reagent participate thyolic, amino, carboxylic groups and hydroxylic group of the thyrosine molecule [14]. By the wool treatment with p,p'-difluor-m,m'-dinitrodiphenylsulphone it appears new cross-linkings in keratin, when the amino group of lysine and phenolic group from thyrosine react.

Halogenated ketones, both aromatic and aliphatic, for instance dichlor-acetone and p-brom-bromacetophenone, react with amino, guanidino or thiolic groups, reticulating the polypeptidic macromolecules.

The keratin is easy reticulated by the wool treatment with carbonyl compounds, the formic aldehyde being a classic keratin reticulant [12]. In the reticulation process with this aldehyde it participates carboxylic group of the glutamic acid and amino or amido groups of the arginine, asparagine and glutamine [15]. With formic aldehyde may react too the amino group of the lysine, the hydroxyl groups of the serine and threonine, the aromatic nucleus of the thyrosine, the nuclei of imidazole or indole [16], but also the peptidic and thiolic groups [17].

There are many another possibilities for keratin reticulation. These possibilities of reticulation, constitute arguments that in wool keratin are amny organic groups, which contribute at this process. In case of using the oxalyl chloride, an organic product much more reactive than those indicated above, undoubtedly that at least the same groups will participate in the reticulation reaction with this reagent.

Because the oxalyl chloride is very reactive, for the wool treatment it was necessary to dissolve this oxalyl chloride in a non-polar dissolvent; we have considered

that such a dissolvent may be carbon tetrachloride.

3. Experimental Part. The raw wool was purified by extraction with carbon tetrachloride (CCl_4) in a Soxhlet apparatus, then it was washed with distiled water at 35-38°C and let to dry at room temperature. The remained impurities was manually removed and finally the wool was again washed with carbon tetrachloride.

A quantity of 5 g purified wool, analytically weighed, was introduced in 300 ml carbon tetrachloride, containing 6 ml oxalyl chloride. Because the oxalyl chloride has 1,5 density, the used solution had a volumetric concentration of 3%. In this way was obtained a concentration in oxalyl chloride with that used in wool dyeing process with aqueous solution of dyes. The oxalyl chloride solution with wool sample is heated at ebullition and mentained 60 minutes. Then, the wool sample is washed with much distiled water and let for natural drying.

Another quantity of 5 g purified wool was treated with 300 ml carbon tetrachloride, having 6 ml oxalyl chloride too; then it is heated at ebullition and it is maintained 120 minutes. Also in this case the wool sample is washed with distiled water and let to dry. After drying, the treated samples with oxalyl chloride have obtained a very small yellowish shade, comparative with the witness sample.

Both the treated wool samples with oxalyl chloride and the witness sample (non-treated wool) were put at many experimental tests, in parallels, to render evident the appeared changes in the chemical structure.

3.1. Solubilization tests. The first solubilization test was made using the urea-bisulphite reactive [5]. The obtained results with this reactive are presented in Table 1; every result represents the average of ten determinations.

Table 1

Wool sample	Solubility, [%]
Witness sample	19.53
Treated wool with oxalyl chloride (60 minutes)	20.90
Treated wool with oxalyl chloride (120 minutes)	20.19

The second solubilization test was using the natrium hydroxyde solution $n/10$, according to H a r r i s and S m i t h's method [18]. The obtained results are presented in Table 2; in this case also every result is the average of ten experimental determinations.

Table 2

Wool sample	Solubility, [%]
Witness sample	24.50
Treated wool with oxalyl chloride (60 minutes)	31.06
Treated wool with oxalyl chloride (120 minutes)	30.27

3.2. Ortho-phenylene-diamine test. It is known that the α-diketonic groups easyly reacts with o-phenylene-diamine [19]. Treated wool samples with oxalyl chloride and a witness sample were put to react with o-phenylene-diamine, in an aqueous medium. The treated wool with oxalyl chloride was coloured in a maroon shade, much more dark than withness sample. Because the o-phenylene-diamine is soluble in pyridine, all the samples were put to extraction with this solvent. After many extractions with

heated pyridine, the withness sample was very much discoloured to yelow, while the treated wool samples have maintained practically the same initial maroon shade.

Another argument to render evident the carbonyl groupe was the treatment with aniline and phenylhydrazine. By heating with aniline, the treated wool appears coloured in dark-yellow shade, but the withness sample appears very little coloured. By heating with phenylhydrazine, the treated wool with oxalyl chloride is coloured in yellow and by further heating it appears a red-cherry shade; in the same conditions the withness sample appears only yellowish.

3.3. Physico-mechanical indices. To render evident the new cross-linkings presence in keratin, we have determined the physico-mechanical indices of the wool fibres, respectively the resistance to tearing and extension. These indices were determined with a Schoper dynamometer. For each wool sample it was made hundred determinations. The resistance to tearing was calculed using the following relation:

$$F = 0.5 + \frac{XG}{100} \text{ gf/fibre}$$

and for the fibre extension calculation, the relation:

$$I = 100\frac{X}{L}$$

In these relations X is the average of the hundred determinations, G represents the pendulum weight, which was 20 g and L is the distance between the dynamometer clamps, respectively the fibre length between clamps; in the present paper the fibre length was 20 mm. The obtained results are indicated in Table 3.

Table 3

Wool sample	Resistance to tearing	Extension
Witness sample	7.72	38.35
Treated wool with oxalyl chloride (60 minutes)	16.03	28.90
Treated wool with oxalyl chloride (120 minutes)	15.75	29.90

The keratin reticulation was evinced by swelling of wool fibres too. On this purpose, both the treated samples with oxalyl chloride and nontreated wool samples were introduced in a natrium carbonate solution, having the pH=10 and were maintained there 12 hours; then it was determined the diameter fibres by means of an optic microscope. The average of many determinations is presented in Table 4.

Table 4

Wool sample	Diameter, [μm]
Witness sample	25.5
Treated wool with oxalyl chloride (60 minutes)	21.8
Treated wool with oxalyl chloride (120 minutes)	22.2

4. The Results Interpretation. The simple fact that the treated wool with chloride appears a little yellowish proves that structural changes in keratin are produced. Considering the functional groups of the keratin which may participate at the reaction with the oxalyl chloride, it is very easy to interpret that there are not formed

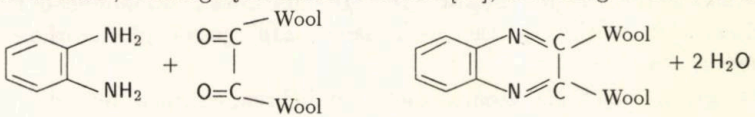
strong chromophoric structures, which can determine a more intense colouring of the treated wool.

The treated wool samples with oxalyl chloride were analytically weighted, before and after treatment, finding an increase in weight of 0.6%. This increase in weight may be explained only if we admit that the keratin has reacted with this organic product, binding it.

The urea-bisulphite solubility indices do not differ much between them, both for the treated samples with oxalyl chloride and for witness sample. These results permit to interpret that the new appeared cross-linkings by wool treating with oxalyl chloride are not stable at reducing action of bisulphite; hence it is not possible to render evident the new cross-linkings in keratin, using this reactive. The small diferences existing between these indices, do not permit us to draw other conclusions.

In the case of solubility test in natrium hydroxyde solution 0.1 n, it takes place a clear superior solubilization of treated wool with oxalyl chloride. This solubilization increase may be explained by a hydrolitic action of the alkaline medium concerning the new cross-linkings, when it may appear new ionized carboxylic groups, which, certainly, contribute to the solubilization process of the keratin.

Because the treated wool with oxalyl chloride is coloured during the treatment with *ortho*-phenylene-diamine and the colour is stable, i.e. it does not disappear by extraction with heated pyridine, this permits to draw the conclusion that this diamine is chemically bound. Indeed, α-diketones react very easyly with *ortho*-phenylene-diamine, forming kynoxaline derivates [19], according to the scheme:



It is observed that by this reaction appears a greater number of conjugated double bonds, consequently it appears a chromophoric system, which determines the colour appearance. Being covalently bound, *ortho*-phenylene-diamine doesn't dissolve any longer in pyridine and by extraction with this solvent, the colour is not changed. The nontreated wool (witness sample) although by treatment with *ortho*-phenylene-diamine is coloured, by extraction with heated pyridine it is very much discoloured; hence, in this case, *ortho*-phenylene-diamine was not chemically bound by the keratin, but only adsorbed.

The fact that the treated wool with oxalyl chloride is colotured by heating with aniline and phenylhydrazine, which colour does not appear for nontreated wool, constitutes an argument for the carbonyl groups existance.

Considering the physico-mechanical indices, it is observed that the resistance to tearing of the treated wool fibres with oxalyl chloride increases notable, comparatively with witness sample. In the same time, the extension is greater for the nontreated wool and much smaller for the treated wool fibre with this reactive. It is known that the resistance to tearing of wool fibre depends on the cross-linkings existence; the more numerous the cross-linkings the greater the resistance. But the cross-linkings presence diminishes much the reciprocal sliding of the polypeptidic

macromolecules, these being better fixed and consequently the fibre extension is smaller; it is diminished. These physico-mechanical indices experimentally obtained permit to consider, logical, that by wool treatment with oxalyl chloride the keratin is reticulated.

Observing the data from Table 4, it results that the diameter of the treated fibres with oxalyl chloride is smaller comparatively with that of witness sample, all the wool samples being maintained in the same conditions for swelling. It is known [7], [20] that the presence of new cross-linkings hinders the wool fibres to swell and consequently the reticulation diminishes their diameter. These determinations prove the fact that by treatment, with oxalyl chloride, the wool keratin is reticulated too.

By observing the obtained data for treated wool only an hour, comparatively with those obtained for the treated wool two hours, it results that there are not notable differences between them. This practical finding permits to interpret that the reticulation process occurs in the first hour of treatment.

By this wool treatment with oxalyl chloride, the wool keratin is enriched with new cross-linkings and consequently with new carbonyl groups.

5. Conclusions. The keratin chemical structure of the wool suggests a lot of possibilities for its reticulation. In this paper it is indicated the keratin reticulation by wool treatment with oxalyl chloride.

Because in the keratin chemical structure there are a great number of free reactive organic groups, which may react with many organic products, the whole wool fibre is generally reactive.

The organic functional groups react with different agents of reticulation, as halogenated ketones or carbonyl compounds, forming new cross-linkings in wool keratin. In the reticulation chemical process it may participate hydroxyl, thiolic, amino, carboxilic amino or peptidic groups.

In case of using oxalyl chloride, a chemical product much more reactive than halogenated or carbonyl compounds, it may be admited that it will participate to the reticulation reaction at least the same functional groups.

The wool treatment with oxalyl chloride is made in a nonpolar solvent, as carbon tetrachloride (CCl_4), which does not react with the reticulation agent.

Using the same organic reactives as aniline, phenylhydrazine and *ortho*-phenylenediamine, the new carbonyl groups presence in wool keratin, respectively the α-diketone group presence, are rendered evident.

The physico-mechanical indices, as for instance the resistance to tearing, extension and fibres diameter constitute arguments, which prove that by wool treating with oxalyl chloride, the keratin is reticulated.

Because there are not great differences between the solubility and physico-mechanical indices for the treated wool with oxalyl chloride only an hour, comparatively with those obtained during two hours of treatment, we can arrive to the conclusion that the reticulation process occurs only in the first hour.

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INTERACŢIUNEA LÂNII CU CLORURA DE OXALIL

(Rezumat)

Prezenţa unui număr mare de grupe funcţionale reactive, legate de resturile laterale ale catenelor polipeptidice din structura cheratinei, determină pentru întreaga fibră de lână o reactivitate ridicată.

Funcţiile organice libere intră în reacţie cu mulţi compuşi, care, uneori, determină reticularea cheratinei. Cercetările efectuate au pus în evidenţă că în procesul de reticulare pot interveni grupe hidroxilice, tiolice, aminice, carboxilice etc. Tratând lâna cu o substanţă deosebit de reactivă, cum este clorura de oxalil, cel puţin aceleaşi grupe vor reacţiona cu acest produs. Se introduc astfel în cheratină grupe α-dicetonice, a căror prezenţă s-a identificat cu anilină, fenilhidrazină şi *o*-fenilendiamină.

Cu ajutorul indicilor fizico-mecanici, respectiv rezistenţa la rupere, alungirea şi diametrul fibrei, se pune în evidenţă apariţia a noi legături transversale în cheratină.

Datele experimentale duc la interpretarea că reacţia lânii cu clorura de oxalil se petrece în prima oră de tratare.

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GRAFTING OF WOOL THROUGH UV RADIATION INITIATION

VI. RHEOLOGICAL CHARACTERIZATION OF WOOL GRAFTED WITH ALKYL- AND HYDROXYALKYL-TYPE ACRYLATED MONOMERS

BY

V. BLAŞCU and AURELIA GRIGORIU

The paper performs a complex rheological characterization of wool grafted by us comparatively with the reference, Romanian wool – type 22.

Stress-relaxation rheological studies have been performed on singular fibers, obtaining total deformation under load, components of elastic recovery, remanent deformation, degree of elasticity, the recovery rate and the yield-recovery curves.

The obtained rheological parameters are correlated with the fibers structures modification induced by grafting polymers.

1. Introduction. Starting with the work reported by S p e a k m a n in 1928 [1], a number of authors have made important contributions to the understanding of the stress relaxation of wool fibers [2],...,[5].

This relaxation is attributed to the breaking of various physical and chemical crosslinks on extension and their reformation with the passage of time. Based on the time scale over which they are effective, these bonds are categorized into three main groups [6]:

– Weak bonds having relaxation times below 0.1 min. including hydrogen bonds and van der Waals and electrostatic forces;

– Bonds of intermediate strength having relaxation times between 0.1 and 10 min., due to disengagement of bonds between matrix and filament components;

— Strong bonds having relaxation times above 10 min., consisting of covalent crosslinkages, mainly disulfide bonds.

These three categories of relaxation mechanisms are referred to as low, intermediate, and long time relaxation processes. The intensity and rate of relaxation depends on test conditions such as temperature, humidity and strain history.

From another viewpoint, it is useful to summarize the prominent molecular processes responsible for relaxation in the three characteristic regions [7]:

– Hookean region: intrahelical bonds and side chain interactions between the helical structure and matrix molecules, mainly disulfide bonds;

– Yield region: tearing apart of the side chain bonds between matrix molecules and helices with simultaneous alignment of matrix chains;

– Postyield region: stretching or opening of covalent crosslinkages in globular matrix proteins.

The rheological phenomena of stress-relaxation type, occurring in wool fibers are quite complex, due to the structural complexity and non-uniformity of the fibrous material from the same group.

As a result of a series of investigations developed along the years in our laboratory, an original methodology for the rheological characterization of wool fibers has been established [8], to be applied in the present study, too.

2. Experimental

2.1. Material. The stress-relaxation rheological studies have been performed on singular fibers of type-22 wool, either as such reference samples or grafted by us with alkyl and hydroxyalkyl acrylated monomers [9], [10]. Similarly with other studies [11], [12], [13], we selected from the experimental programs samples with low, medium and high degree of grafting. The samples' codification has been given in [11].

The investigations involved a device operating according to the electromagnetic principle, with a high precision in the measurement of the deformation's modifications in time.

2.2. Method. Evidencing of the viscoelastic characteristics of the wool fibers involved several yield and relaxation experiments, based on stressing of the individual fibers with constant load, for a determined time interval. The modification of deformation, under the action of the static force (P_s, cN), was followed along with the fiber's recovery, when stress is over.

The main testing conditions were the following:

– utilization of the individual fibers whose diameter corresponded to an average thickness of ± 2 μm;

– stress with two forces, one corresponding to the elastic domain and the other to the viscoelastic one (as established by the effort-elongation curves);

– stress (t_1) and, respectively, relaxation durations (t_2)=15 min.;

– the number of determinations/sample ranged between 5 and 10, as depending on the degree of non-uniformity observed.

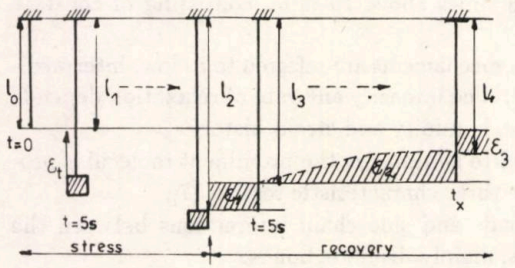

Fig. 1. The fiber stress-recovery stages.

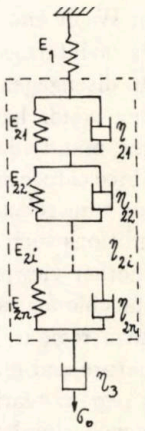

Fig. 2. The generalized Kelvin-Voigt model in series with a simple Maxwell model [15].

A schematic representation of the fibers' dimensional modifications in length, versus some different stress-recovery stages is given in Fig.1 [15].

The average values of deformation recorded during both stress and recovery stages permitted the calculation of the following parameters:

a) total deformation under load, as a result of a 15 min. stress (ε_t, %). Total deformation ε_t up to time t_k, under the action of the stress force, will be given by the three types of deformation of the viscoelastic bodies:

$$\varepsilon_t = \varepsilon_e + \varepsilon_{v-e} + \varepsilon_c,$$

where: ε_e – elastic deformation; ε_{v-e} – viscoelastic deformation; ε_c – flow deformation or, according to the generalized Kelvin-Voigt model (Fig.2):

$$t = \frac{\sigma_0}{E_1} + \sum_{i=1}^{n} \frac{\sigma_0}{E_{2i}} \left(1 - e^{-\frac{t}{t^*}}\right) + \frac{\sigma}{\eta_3} t,$$

where: $t^* = \eta_i / E_i$, delay or yield time.

b) components of elastic recovery:

– instantaneous elastic recovery (ε_1, %)

$$\varepsilon_1 = \frac{l_2 - l_3}{l_2 - l_0} \cdot 100$$

– low or delayed elastic recovery (ε_2, %)

$$\varepsilon_2 = \frac{l_3 - l_4}{l_2 - l_0} \cdot 100$$

c) remanent deformation (ε_3, %)

$$\varepsilon_3 = \frac{l_4 - l_0}{l_2 - l_0} \cdot 100$$

d) degree of elasticity (G_e, %). The capacity of elastic recovery is expressed through the elasticity degree, which represents the weight of the total elastic (both instantaneous and delayed) recovery from the total deformation recorded when the stress is removed:

$$G_e = \varepsilon_1 + \varepsilon_2 \qquad \text{or} \qquad G_e = \frac{l_2 - l_4}{l_2 - l_0} \cdot 100$$

e) the recovery rate, V_r (%/min.), calculated with relation:

$$V_r = \frac{G_e}{15 \text{ min.}}$$

f) the yield-recovery curves $\varepsilon = f(t)_p$ have been plotted.

3. Results and Discussions. The average values of the rheological parameters of the samples analyzed are listed in Table 1, and the yield-recovery curves in Figs.3,...,6.

Table 1

Evolution of the Rheological Characteristics

No. of sample	P_s cN	$(P_s/P_r)100$	ε_t	ε_1, %	ε_2, %	ε_3, %	G_e, %	V_r, %/min.
0	3	24.19	6.9	40.01	24.36	32.63	64.37	4.29
	6	48.38	8.4	32.76	21.36	45.88	54.12	3.60
I.1	3	16.94	4.1	45.76	28.81	25.43	74.57	4.97
	6	33.88	6.9	38.23	25.30	36.47	63.53	4.23
I.2	3	13.00	3.7	47.51	29.22	23.27	76.73	5.11
	6	26.00	6.5	41.18	26.71	32.11	67.89	4.52
I.3	3	11.91	3.5	49.16	32.10	18.74	81.26	5.41
	6	23.82	6.2	42.63	28.45	28.92	71.08	4.73
II.1	3	17.64	6.3	42.60	27.37	30.03	69.97	4.66
	6	35.28	7.7	35.17	23.81	41.02	58.98	3.93
II.2	3	13.19	5.5	44.32	28.27	27.41	72.59	4.83
	6	26.38	6.5	38.55	25.61	35.84	64.16	4.27
II.3	3	12.17	4.3	46.02	31.02	22.96	77.04	5.13
	6	24.34	6.4	39.36	27.70	32.94	67.06	4.47
III.1	3	18.18	6.3	41.39	26.44	32.17	67.83	4.52
	6	36.36	7.9	34.28	22.82	42.90	57.10	3.80
III.2	3	13.77	5.8	43.11	27.11	29.77	70.22	4.68
	6	27.54	7.2	37.03	24.18	38.79	61.21	4.08
III.3	3	12.60	5.4	44.82	29.76	25.42	74.58	4.97
	6	25.20	7.0	37.70	26.72	35.58	64.42	4.29
IV.1	3	17.80	6.2	41.87	27.00	31.13	68.87	4.59
	6	35.60	7.8	35.08	23.20	41.72	58.28	3.88
IV.2	3	12.87	5.7	43.83	27.81	28.36	71.64	4.77
	6	25.74	7.3	37.87	24.97	37.16	62.84	4.18
IV.3	3	12.29	4.2	45.19	30.55	24.26	75.74	5.04
	6	24.58	6.9	38.18	27.02	34.80	65.20	4.34
V.1	3	21.39	6.7	40.78	26.00	33.22	66.78	4.45
	6	42.78	8.0	33.92	22.40	43.68	56.32	3.75
V.2	3	17.73	6.1	42.90	26.80	30.30	67.70	4.51
	6	35.46	7.4	36.60	23.77	39.63	60.37	4.02
V.3	3	13.19	5.6	44.10	28.75	27.15	72.85	4.85
	6	26.38	7.3	37.80	25.94	36.26	63.74	4.24
VI.1	3	21.88	6.8	40.59	25.28	34.13	65.87	4.39
	6	43.76	8.1	33.83	22.00	44.17	55.83	3.72
VI.2	3	18.18	6.2	42.11	26.16	31.73	68.27	4.55
	6	36.36	7.7	35.40	23.32	41.28	58.72	3.91
VI.3	3	13.55	5.7	43.28	28.10	28.62	71.38	4.75
	6	27.10	7.5	36.75	25.30	37.95	62.05	4.13

From the analysis of the values obtained for the recovery time (Table 2), calculated from experimental date and from the rheological equation of the recovery process [16]:

$$t_r = \frac{\varepsilon_r(5'') - 0.2 \cdot 10^{-2}}{2\beta_r' \cdot \sigma^{\eta_r}}$$

on following the values obtained in the determination of total deformation under load, of the instantaneous elastic recovery (ε_1), of delayed elastic recovery (ε_2), of remanent

deformation (ε_3) and of the degree of elasticity (G_e), the following conclusions may be drawn:

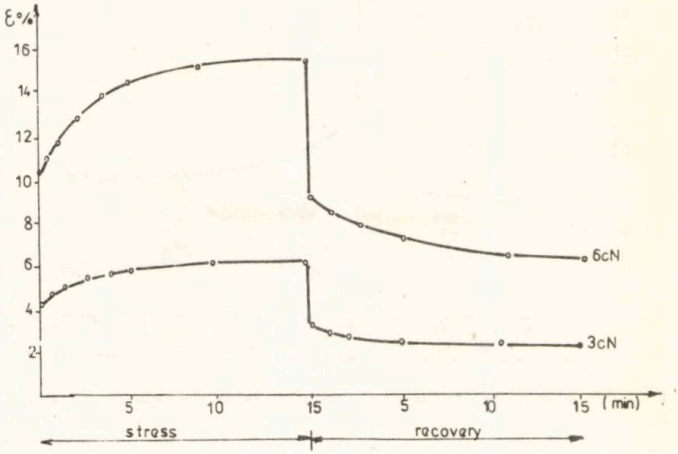

Fig. 3.– The yield-recovery curves for wool reference sample.

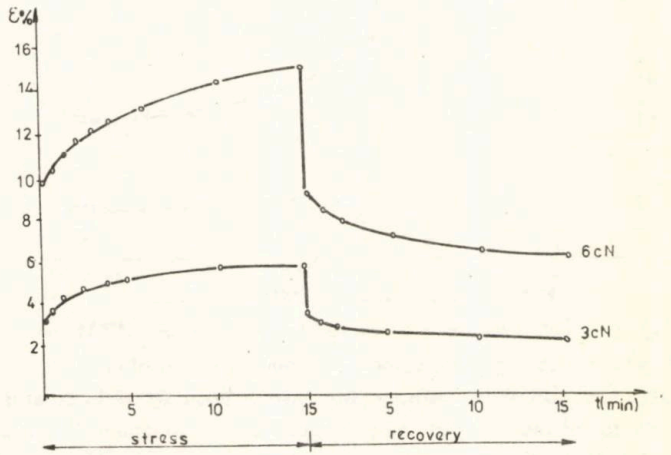

Fig. 4.– The yield-recovery curves for I.3 (wool-g-EA) sample.

– for the same stress load, increase of duration induces decrease of elastic recovery and, consequently, the degree of elasticity, alongwith increase of remanent deformation;

– for the same stress duration, but for increasing stress forces (3, 6 cN), the same decreasing tendency of the elastic recovery capacity is observed, in parallels with the increase of remanent deformation;

– decreases of the recovery capacities are more pronounced when the stress force increases, for the same duration of stress, than when the force and the stress duration are kept constant.

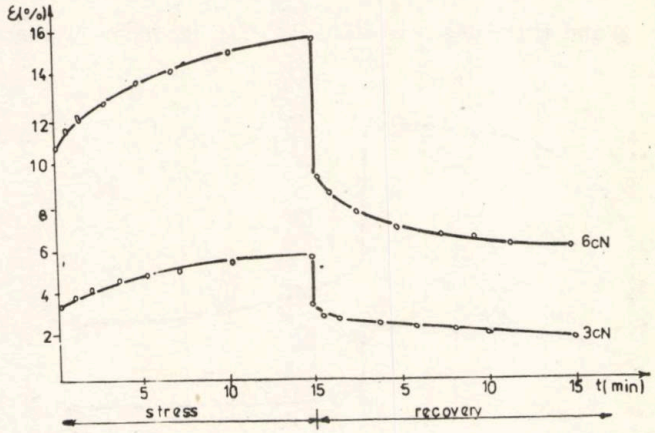

Fig. 5.– The yield-recovery curves for III.3 (wool-g-BA) sample.

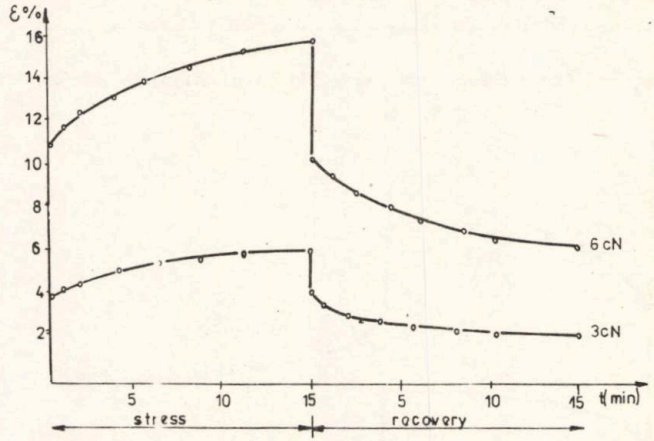

Fig. 6.– The yield-recovery curves for VI.3 (wool-g-HBA) sample.

Analysis of the recovery time values obtained in the applied experimental conditions evidences their increase, with the increase of both stress force and duration.

More pronounced increases of the recovery time are mentioned again in the case of increasing forces stresses, comparatively with the increase of the duration of stress exercised by a constant force.

The experimental date show an increase of the elastic deformations (ε_1 and ε_2) and a decrease of the remanent one (ε_3), alongwith an increase of the elasticity degree (G_e) and of the recovery rate (V_r) for the grafted samples, comparatively with the reference sample; also, more intense evolution tendencies are noted for higher grafting degrees.

As to the influence of the grafting monomer, the above mentioned evolutions are strongly dependent on its nature, and, implicitly, on the grafting degree.

Evolution of the rheological indices depends on the presence of the substituent from the monomer (more or less bulky) as well as on its polarity (the hydroxyalkyl

Table 2
Evolution of the recovery times.

No. of sample	P_s cN	Stress time, T_s, min.				No. of sample	P_s cN	Stress time, T_s, min.			
		1	5	10	15			1	5	10	15
		Recovery times, T_r, min.						Recovery times, T_r, min.			
0	3	25	27	28	30	IV.1	3	16	17.5	19	20.5
	6	28	30	32	34		6	18	19.5	21	23
I.1	3	15	17	19	21	IV.2	3	15	17	18.5	21
	6	17	19	21	23		6	17	19	20.5	22
I.2	3	14	16	18	20	IV.3	3	14	16.5	17.5	19.5
	6	16	18	20	22		6	16	18	20	21.5
I.3	3	13	14.5	15.5	17	V.1	3	17.5	19.5	21.5	23.5
	6	15	16.5	17.5	19		6	19.5	21	22.5	24.5
II.1	3	15.5	17	19	21.5	V.2	3	16.5	18.5	20.5	22
	6	17.5	19	21	22.5		6	18.5	20	21.5	23
II.2	3	14.5	16	17.5	19.5	V.3	3	15.5	17	18.5	21
	6	16.5	18	19.5	21.5		6	17.5	19	21.5	23.5
II.3	3	13.5	15.5	17.5	19.5	VI.1	3	18	20	22	24.5
	6	15.5	17	19	22		6	20	21.5	23.5	25.5
III.1	3	16.5	19	21	23.5	VI.2	3	17	19.5	22.5	25
	6	18.5	20	21.5	24		6	19	20.5	23.5	26
III.2	3	15.5	17	18.5	21.5	VI.3	3	16	18.5	22	24.5
	6	17.5	18.5	20	22		6	18	20	22.5	25.5
III.3	3	14.5	16.5	18.5	20.5						
	6	16.5	18.5	20.5	22.5						

acrylated monomers induce lower decreases of the rheological characteristics, probably due to the involvment of the -OH fraction in additional hydrogen bonds from the wool fiber's structure).

4. Conclusions. A corroborative analysis of the obtained experimental data permits drawing of the following conclusions:

– increase of the stress force causes profound structural modifications both at the level of the reference fiber and of the grafted ones, as evidenced by increase of the recovery time;

– the behaviour on both direct and reverse yield of the unmodified and grafted wool fibers evidences that, in all cases taken into study, total deformations under load are higher for the reference fibers, followed by their decrease with the increase of the grafting degree;

– depending on the nature of the grafting monomer, such decrease occurs in the following order: $EA > PA > HEA > BA > HPA > HBA$;

– the capacity of elastic recovery is lower for the reference samples, comparatively with the grafted ones; the same aspect is evidenced by the values of the recovery time, higher for the reference fibers, while the recovery rate increases progressively starting from the nongrafted to the fibers grafted with ethyl acrylate, for a maximum grafting degree;

– for the same monomer, the mechano-rheological indices are improved with the increase of the grafting degree.

All the above observations agree with the experimental values obtained for the

physico-mechanical indices of the wool fibers modified through grafting in our laboratories [12], [13].

The more pronounced viscoelastic effects observed in the reference wool sample, comparatively with the one grafted with alkyl and hydroxyalkyl acrylated monomers by UV irradiation, may be mainly explained by the structural differences, especially the fibers' organization and the bilateral structure.

In the ortho-cortical regiones, a more pronounced fibrils' disorientation may be observed, and also a higher density of the bulky functional groups [17],...,[19]. In dry state, the matrix has a vitrous structure, as a result of the interchain links [20].

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GREFAREA LÂNII PRIN INIŢIERE CU RADIAŢII UV

VI. Caracterizarea reologică a lânii grefate cu monomeri alchil şi hidroxialchil acrilaţi

(Rezumat)

Se caracterizează complex, din punct de vedere reologic, fibrele de lână martor şi cele grefate. Caracteristicile reologice precum: componentele elastice, vitezele de revenire, curbele „solicitare–revenire" sunt obţinute prin experimentări de tensiune–relaxare efectuate asupra fibrelor singulare.

Sunt corelate mărimile reologice obţinute cu modificările în structura fibrelor imprimate de polimerii de grefare.

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Secţia VIII
TEXTILE. PIELĂRIE

GRAFTING OF WOOL THROUGH UV RADIATION INITIATION

VII. STRUCTURAL ANALYSES OF WOOL FIBERS GRAFTED WITH ALKYL- AND HYDROXYALKYL-TYPE ACRYLATED MONOMERS

BY

AURELIA GRIGORIU, V. BLAŞCU and GEORGE E. GRIGORIU

The Romanian wool fibers 22-type grafted by us through UV radiation initiation, with alkyl and hydroxyalkyl-type acrylated monomers were subjected at multiple structural analyses investigations.

The results obtained by means of scanning electron microscopy, optical birefringence, IR and IR-ATR spectroscopy and gel permeable chromatography led to important conclusions about reference and chemically-modified wool fibers.

1. Introduction. Although, at laboratory level, numerous achievements have been recorded in the domain of wool fibers grafting, technological, economic and ecological reasons restricted their industrial application [1], [2].

Quite frequently, polymers have been employed in the control of wool's felting. The first attempts have been made as early as 1946 [3], although the large-scale application of polymers in such domain occurred only 20 years later [4]. In time, the interest increased with improving the process' efficiency, lowering of costs, etc. At present, around 50 polymeric treatments, quite accessible commercially, are known (e.g. Hercosett/Hercules/ or Synthappret/Bayer/ type products).

Along the years, several reaction systems have been utilized for increasing the efficiency and selectivity of wool's grafting [1].

Wool's grafted copolymers have been subjected to physico-chemical, mechanical, rheological, etc. analyses, which permitted to study the modification, either positive or negative, of the fibers' properties [1], [5],...,[8].

The methods of structural analysis: scanning or transmission electronic microscopy [1], [2], optical birefringence [9], X-ray diffraction [10], [11], molecular mobility through magnetic resonance studies (RMN) [12], thermogravimetry (TGA) [13],...,[15], differential calorimetry (DSC) [16], [17], IR absorption [1], [18], investigate thoroughly the microstructure of reference and modified wool fibers.

Only a limited amount of work has been reported in the literature on the birefringence of wool fibers [19],...,[23], perhaps because of an incomplete understanding of its structure, particularly of the amorphous phase, and also due to difficulties associated with accurate measurements of birefringence.

The samples of Romanian, 22-type wool, chemically modified by grafting with alkyl- and hydroxyalkyl-acrylated monomers from homologous series [24], [25] have

been subjected to determinations of structural analysis by means of: scanning electron microscopy; optical birefringence; IR and IR-ATR spectroscopy; gel permeable chromatography (GPC).

2. Experimental. Materials. Installations. Methods. The structural analyses have been performed on both standard and chemically modified (through grafting) wool fiber samples. As in our previous papers [5],...,[8], from the experimental programs there have been selected samples with low, average and high grafting degree. The samples' codification has been given elsewhere [5].

The experimental determinations involved the following stages:

– for scanning electron microscopy, photographs have been taken with a Tesla-Type BS 300 electronic microscope. Prior to the analysis, the samples have been metallized in vacuum, with Ag, according to the principle of cathodic atomization, then blocked mechanically on the Al metallic suports, and contacted electrically with Ag colloidal paste. The working parameters involved were the following: $U_{\text{acceleration}}$=20 kV, inclination angle=60°.

A thorough electronomicroscopic study, aimed at evidencing the internal structure's modification, was based on the technique of fiber's fracturation in liquid nitrogen, in a special fracturation installation.

– for the birefringence studies we first selected the samples on the basis of dimensional uniformity, i.e., fibers with a coefficient of variation of diameter less than 10%. We then measured the birefringence of selected fibers using the compensator method, and selected those fibers that had birefringence values close to the average of each wool type for our investigation. We measured birefringence with the aid of a polarizing microscope Amplival pold. (Karl Zeiss Jena) fitted with a compensator and equipped with a fiber rotator device. The actual optical path, i.e., thickness of the fiber at the point of measurement, was measured to an accuracy of 0.1 μm. Fifteen observations were taken on each fiber over a test length of 15 mm, and the birefringence Δn was calculated in each case using the relation: $\Delta n = \Delta d/d$, where Δd is the path difference and d is the path length, in nm. The average of fifteen measurements at 25±1°C was taken as the birefringence, which was accurate to within ±0.0002 in general, the data were reproducible to an accuracy of 2% of the measured value.

– IR-ATR spectrographic analyses have been recorded with an IR-SPECORD M80 (Karl Zeiss Jena) spectrophotometer, on both reference and grafted wool fabrics, under the experimental conditions applied for the obtainment of a maximum degree of grafting (see also [5], [6]). An ATR crystal of KRS-5 (bromide-thallium iodide) with the following characteristics: thickness 3.5 mm, number of internal reflexions 14, crystal angle 45°has been employed.

– IR spectrographic analyses of the polymer grafted on wool fibers, remaining after dissolution of the support wool in 6N HCl, comparatively with the homopolymer obtained through thermal polymerization, have been recorded on solid films obtained from the solutions of the two polymers in acetone, deposited on KRS-5 crystal. Hydrolysis of the grafted wool samples was performed with 6N HCl solutions, at 115°C, for 24 hours, keratine passing into solution and leaving a polymer viscous

mass, which was washed several times, for the total removal of the acid traces, dissolved in benzene and purified through 2 precipitations.

GPC chromatograms have been obtained on a WATERS installation at 150°C, with a μ-Styragel columns (porosity values ranging between 10^2-10^6 Å) which employ tetrahydrofurane (THF) at 30°C.

The reactives utilized were of purity, 98-99.9%, supplied by Merck, Aldrich, Jennsen.

3. Results and discussions. The electromicroscopic images of the surface of the reference and grafted at a maximum grafting degree wool samples are presented in Figs.1,...,7.

Fig. 1.– Reference sample Longitudinal, x2500.

Fig. 2.– Wool-g-EA, Sample I.3 Longitudinal, x2500.

Fig. 3.– Wool-g-PA, Sample II.3 Longitudinal, x2500.

Fig. 4.– Wool-g-BA, Sample III.3 Longitudinal, x2500.

Morphologically, the aspect of the grafted fibers' surface is not significantly different from that of the reference samples, even if at high grafting degrees, which means that most part of the grafted polymer placed in the region of keratine matrix, among microfibrils. The external surface of the grafted fiber and its diameter are nevertheless different from those of the reference, the tendency of the scales' covering and of the diameter's increase, being observed.

The effect of the polymer's deposition on the scales' surface and, especially, among the scales, is mentioned.

The fractions obtained evidence modifications of the fraction's shape, starting

Fig. 5.– Wool-g-HEA, Sample IV.3 Longitudinal, x2500.

Fig. 6.– Wool-g-HPA, Sample V.3 Longitudinal, x2500.

Fig. 7.– Wool-g-HBA, Sample VI.3 Longitudinal, x2500.

Fig. 1'.– Reference sample Fracture, x2500.

Fig. 2'.– Wool-g-EA, sample I.3 Fracture, x2500.

Fig. 3'.– Wool-g-PA, sample II.3 Fracture, x2500.

from the reference sample (Fig.1') up to the one possessing the highest amount of grafted polymer (Fig.7').

Fig. 4'.– Wool-g-BA, sample III.3 Fracture, x2500.

Fig. 5'.– Wool-g-HEA, sample IV.3 Fracture, x2500.

Fig. 6'.– Wool-g-HPA, sample V.3 Fracture, x2500.

Fig. 7'.– Wool-g-HBA, sample VI.3 Fracture, x2500.

In the case of the reference sample, the cortex, the main part of the α-keratinic fibers, is constituted of cortical cells containing long filaments (microfibrils) oriented in parallel on the fiber's direction, and included in the rich-in-sulphur matrx. The dimension of the microfibrils' cross section ranges between 6 and 8 nm [9]; they evidence a good cross elasticity and they do not break simultaneously, so that several unfractured microfibrils remain (Fig.1'). With the increase of the content of grafted polymer inside the matrix, structure's "rigidization" occurs, while the behaviour at fracture tends to approach the "macaroni"-type breaking (Figs.2',...,7').

By the technique of fracturing, electronic microscopy evidences the microfibrils' ordered nature, and no well-defined organization inside the matrix. The same conclusions have been drawn from X-ray diffraction studies, as well [21].

The results of the optical birefrigence measurements are listed in Table 1.

The results refer only to the reference sample and to the six grafted ones, characterized by maximum grafting degrees, as the samples with lower values of this parameter have a birefringence sensibly equal with that of the samples discussed.

It was observed that increase of the grafting degree lowers the value of birefringence, which evidences the tendency of stabilization around a grafting degree,

Table 1
Values of Optical Birefringence

Sample	Optical birefringence, Δn
0	0.010
I.3	0.009
II.3	0.009
III.3	0.009
IV.3	0.009
V.3	0.009
VI.3	0.009

G=20%.

As optical birefringence may be used as a measure of both molecular orientation and cristallinity, it becomes obvious molecular orientation decreases slightly, below 1%, after grafting.

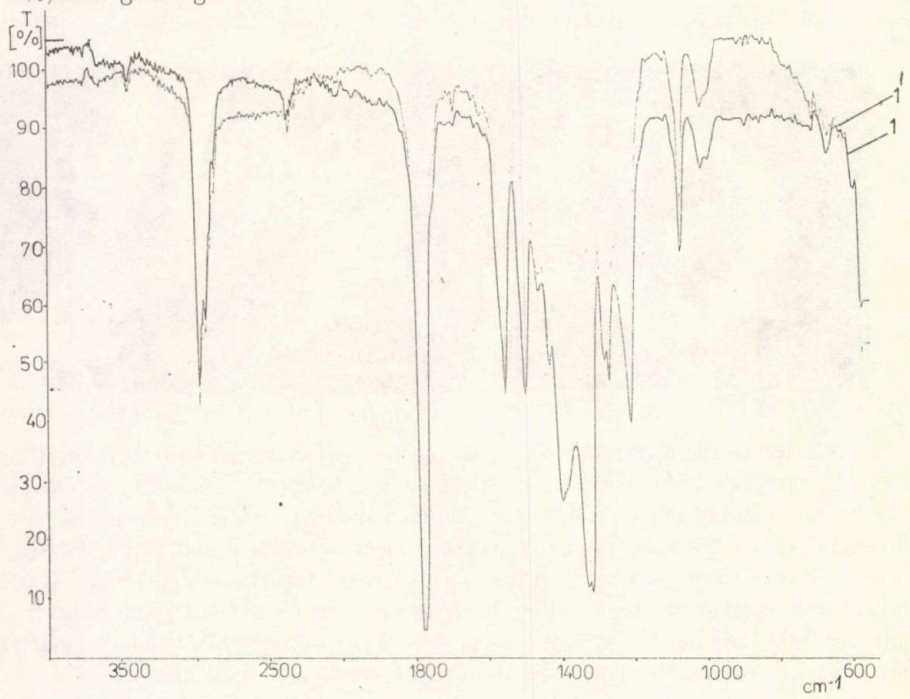


Fig. 8.– Wool-g-EA.

Analysis of IR spectra (Figs.8,...,13) evidences absorptions bands characteristics to certain groups of atoms [26],...,[30] (see Tables 2, 3 and 4) (1 – polymer extracted from grafted wool; 1' – homopolymer).

IR spectra of the polymers isolated by dissolution of the grafted wool in 6N HCl have the absorption bands characteristic for PEA, PPA, PBA, PHEA, PHPA and PHBA and are similarly with that of the homopolymers obtained through radicalic polymerization of the correspondent monomers.

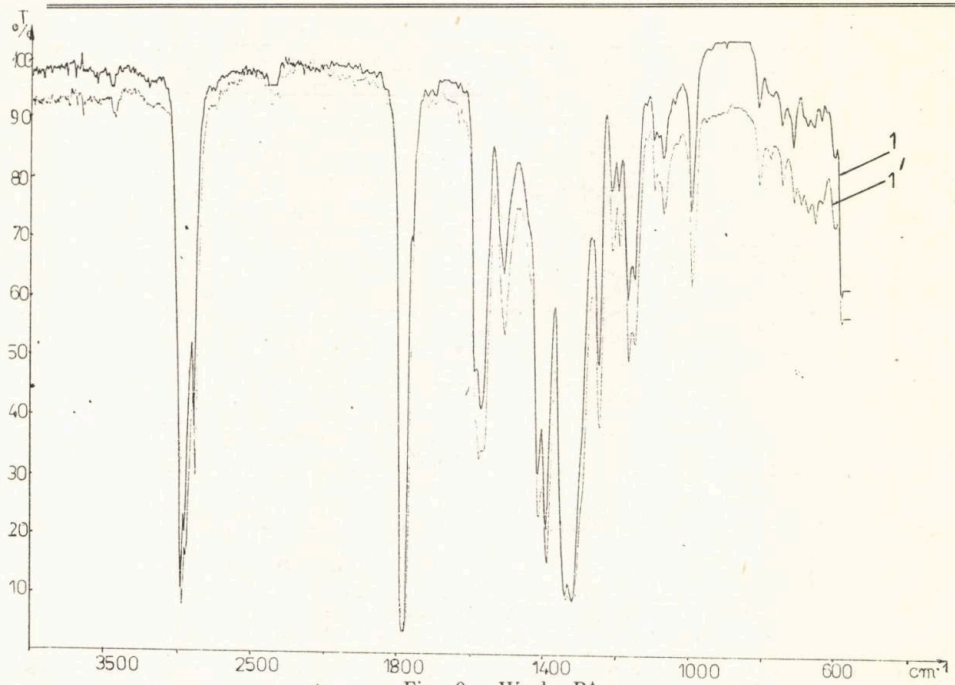


Fig. 9.– Wool-g-PA.

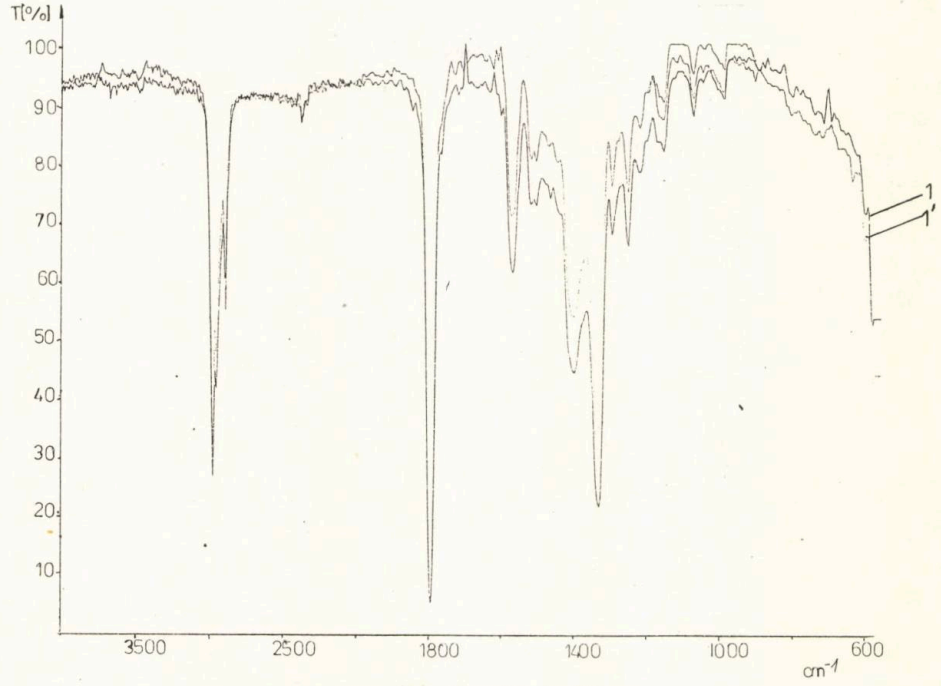


Fig. 10.– Wool-g-BA.

Table 2

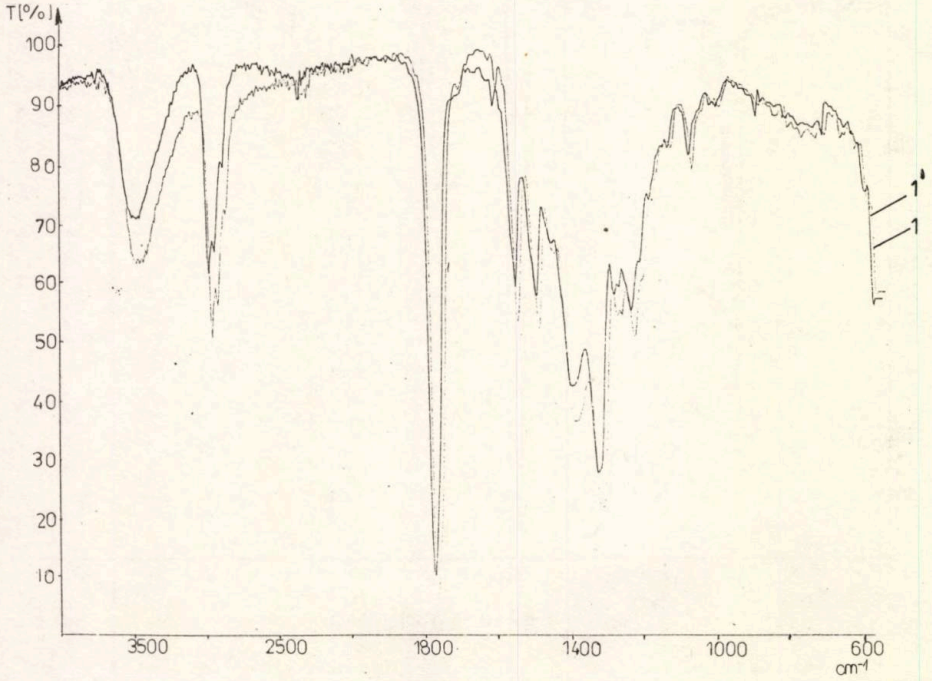
Polyethyl Acrylates. Interpretation of the IR Spectra

Polyethyl acrylate		Polyhydroxyethyl acrylate	
cm^{-1}	Assignment	cm^{-1}	Assignment
–	–	3500	ν(OH)
2985	$\nu_a(CH_3)$		
2940	$\nu_a(CH_2)$	2940	$\nu_a(CH_2)$
2885	$\nu_s(CH_3),\nu_s(CH_2),\nu$(CH)	2880	$\nu_s(CH_2),\nu$(CH)
1735	ν(C=0)	1735	ν(C=0)
1475^u	$\delta_a(CH_3)$		
1465 1450 1400^u	$\delta(CH_2)$	1450	$\delta(CH_2)$
1380	$\delta_s(CH_3)$		
1260 1240^u 1180 1160	O ‖ ν(C–O–C)	1260 1240 1170	O ‖ ν(C–O–C)
1120 1100	Ethyl	1120 1100	Hydroxyethyl
1025	O ‖ ν(C–O–C)	1050 1020	O ‖ ν(C–O–C)
855 785 755	Ethyl	850	Hydroxyethyl

Legend: u – shoulder, ν – valency vibration (ν_s – symmetrical, ν_a – asymmetrical), δ – deformation vibration (δ_s – symmetrical)

For obtainment of the suplimentar informations by IR spectrographic analyses have been recorded the spectra IR for a wool fabric realized from the same fibers, wool-type 22.

Fig. 11.– Wool-g-HEA.



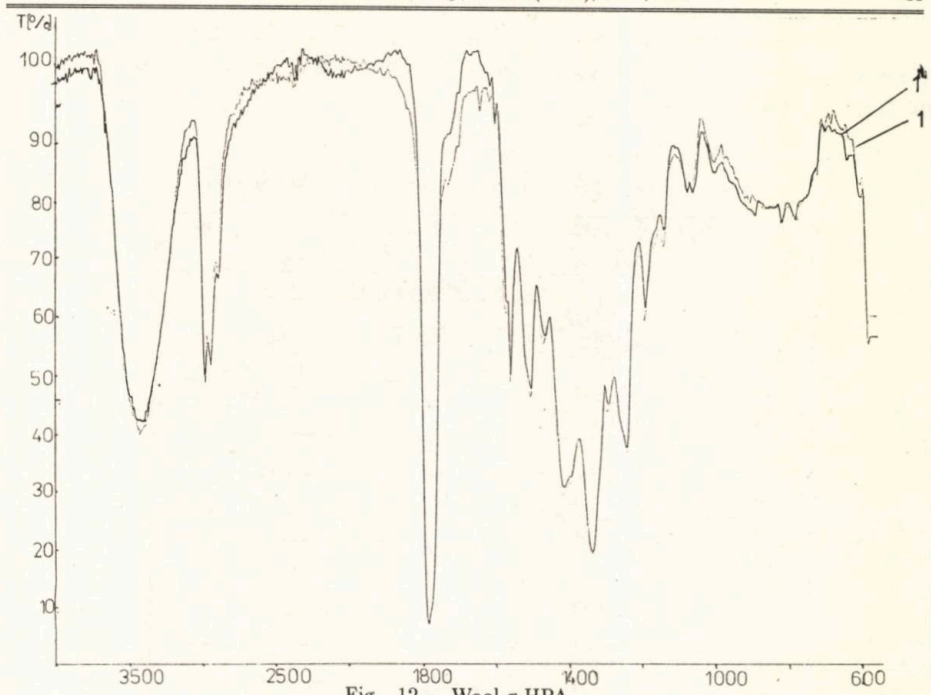


Fig. 12.– Wool-g-HPA.

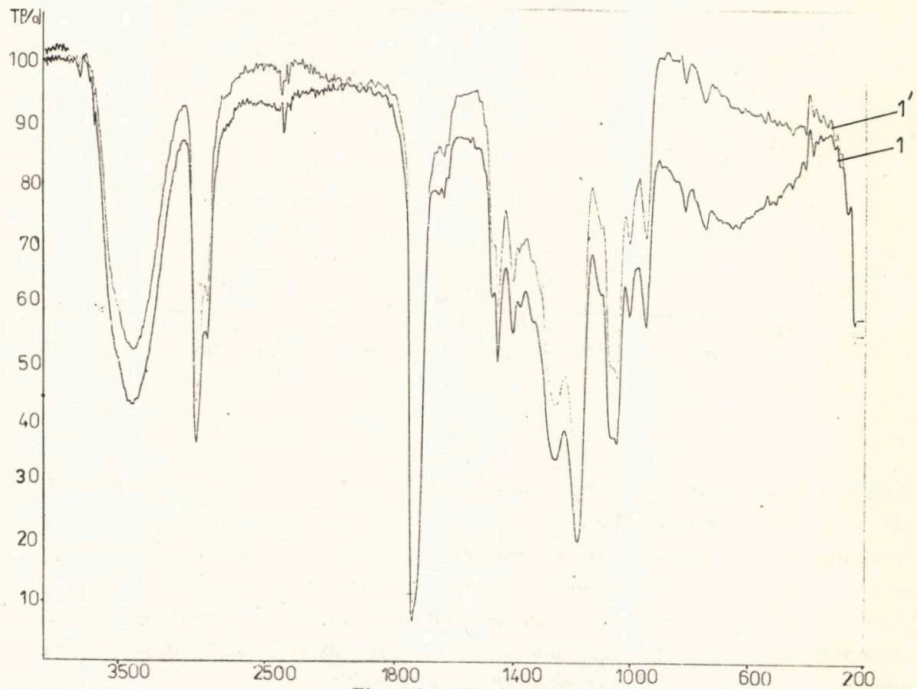


Fig. 13.– Wool-g-HBA.

For IR-ATR spectra have been recorded: *1* – for the standard fabric; *2* – for the monomer (HBA); *3* – for the impregnated fabric with HBA; *4* – for the impregnated and polymerized fabric.

Table 3

Polypropyl Acrylates. Interpretation of the IR Spectra

Polypropyl acrylate		Polyhydroxypropyl acrylate	
cm^{-1}	Assignment	cm^{-1}	Assignment
–	–	3430	ν(OH)
2970	$\nu_a(CH_3)$		
2940	$\nu_a(CH_2)$	2945	$\nu_a(CH_2)$
2880	$\nu_s(CH_3)$,$\nu_s(CH_2)$,ν(CH)	2890	$\nu_s(CH_2)$,ν(CH)
1735	ν(C=0)	1735	ν(C=0)
1475^u	$\delta_a(CH_3)$		
1465 1450 1400^u	$\delta(CH_2)$	1465^u 1455 1400^u	$\delta(CH_2)$
1380	$\delta_s(CH_3)$		
1270 1240 1175 1155	O || ν(C–O–C)	1270 1240^u 1175	O || ν(C–O–C)
1120^u 1065	propyl	1120 1075^u 1055	hydroxypropyl
  1020	O || ν(C–O–C)	 995	O || ν(C–O–C)
1000 965 945 900 880 845 800 745	propyl	985^u 930 850 830 760	hydroxpropyl

Legend: u – shoulder, ν – valency vibration (ν_s – symmetrical, ν_a – asymmetrical), δ – deformation vibration (δ_s – symmetrical)

The four spectra have been reduced and superposed (Fig.14). The characteristic bands being centralized in Table 5.

The apparent weight-average molecular weight $\overline{M}_w$, apparent number-average molecular weight $\overline{M}_n$, and the polydispersity coefficient $I = \overline{M}_w/\overline{M}_n$ of the polyacrylates isolated after hydrolysis of the grafted wool and of the corresponding polymers were determined by gel permeation chromatography (GPC), using polystyrene standards for calibration. The results are given in Table 6.

Table 4

Polybutyl Acrylates. Interpretation of the IR Spectra

Polybutyl acrylate		Polyhydroxybutyl acrylate	
cm^{-1}	Assignment	cm^{-1}	Assignment
–	–	3400	ν(OH)
2965	$\nu_a(CH_3)$		
2940	$\nu_a(CH_2)$	2960	$\nu_a(CH_2)$
2885	$\nu_s(CH_3),\nu_s(CH_2),\nu(CH)$	2885	$\nu_s(CH_2),\nu(CH)$
1735	$\nu(C{=}O)$	1735	$\nu(C{=}O)$
1470	$\delta_a(CH_3)$		
1462 1452 1400	$\delta(CH_2)$	1465 1455 1400	$\delta(CH_2)$
1380	$\delta_s(CH_3)$		
1260 1245 1170	O ‖ ν(C–O–C) butyl	1250 1170	O ‖ ν(C–O–C)
1120 1070		1065	hydroxybutyl
1030	O ‖ ν(C–O–C)	1045	O ‖ ν(C–O–C)
945 845 740	butyl	1000 945	hydroxybutyl

Legend: u – shoulder, ν – valency vibration (ν_s – symmetrical, ν_a – asymmetrical), δ – deformation vibration (δ_s – symmetrical)

It seems that $\overline{M}_w$ and $\overline{M}_n$ values of the grafted polyacrylates and polyhydroxyacrylates are lower than the corresponding homopolymers. This is probably due to the fact that the copolymerization taking place at the fiber surface is more sterically hindered than the homopolymerization. This may be also due to the fact that on the fiber surface the rate of termination (mainly disproportionation for these monomers) would be expected to be higher than it would be in homopolymerization, since radicals are in close proximity at the fibers. The high values of the polydispersity coefficient indicate that initiation sites of substantially different reactivity are being created and that side reactions are taking place during the polymerization of acrylates in this heterogeneous system.

4. Conclusions. Several methods for investigating the structure of both reference and chemically-modified wool fibers through copolymerization grafted with alkyl- and hydroalkyl acrylated monomers have been applied.

A thorough characterization of the structure has been performed by the corroboration of the results obtained by several methods.

Structural analyses have evidenced that grafting took place both on the fibers' surface, but, more intensely, inside them.

The results of these investigations agree with those devoted to the physico-chemical and mechano-rheological properties discussed in previous papers [5],...,[8].

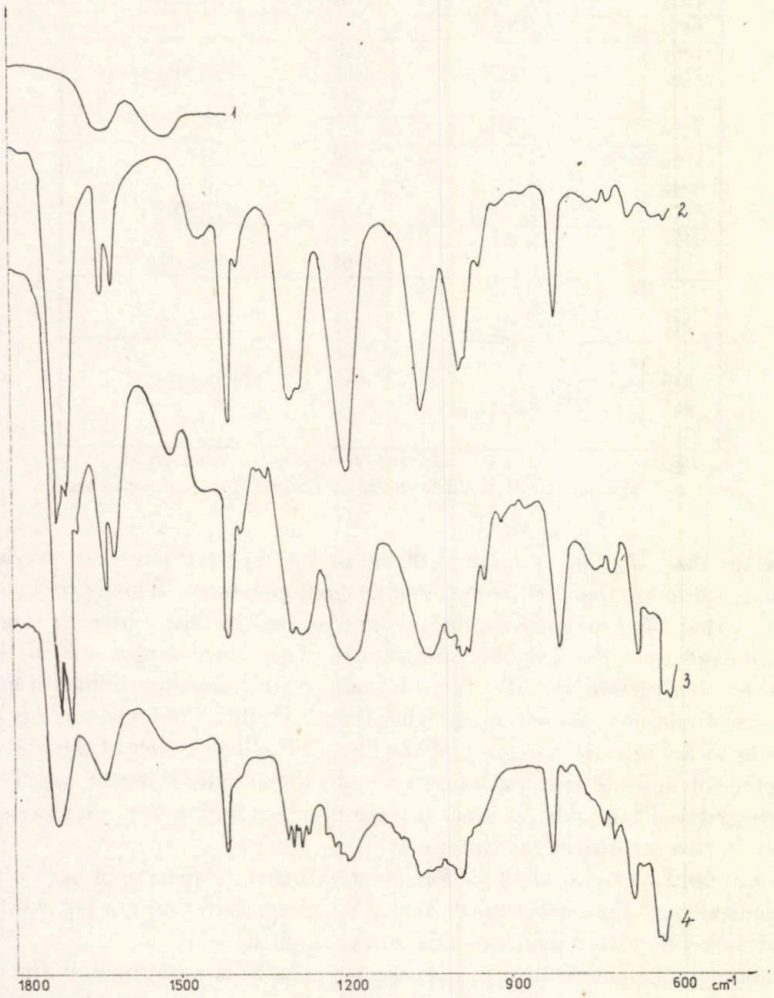


Fig. 14

Table 5

Interpretation of the IR-ATR Spectra

Nr. crt.	Sample	Wave number, cm^{-1}	Characteristic band
1	Wool	1640	Amide I $\nu(\rangle C=O)$
		1535	Amide II $\delta(\rangle NH)$; ν(C-N)
2	Hydroxybutyl acrylate (monomer)	1725	ν(C=O)
		1640	
		1625	Acrylates, ν(C=C)
		1415	$\delta(CH_2)$
		1300	O
		1280^u	‖
		1200	ν(C–O–C)
		1065	Hydroxybutyl
			O
			‖
		1050^u	ν(C–O–C)
			H
			|
		990	R–C=CH_2, Hydroxybutyl
		950^u	Hydroxybutyl
			H
			|
		815	$\gamma(CH_2)$ from H_2C=C–R
		750	
		670	
3	Wool impregnated with hydroxybutyl acrylate (monomer)	The same (summed) absorption bands as for 1 and 2, appear	
4	Wool impregnated with hydroxybutyl acrylate and UV irradiated in the experimental conditions presented in [20]	The bands specific to acrylates decrease in intensity, the tendency of their widening being observed, which indicates the disappearance of the double bonds through photografting. Over the absorption bands characteristic to wool, the absorption bands of PHBA are superposed, a sign of occurrence of grafting on the substrate.	

Legend: u – shoulder, ν – valency vibration, δ and γ – deformation vibration

Table 6

Molecolar Weight of Grafts and of the Similar Homopolymers

Polymer	Polymers isolated from wool's hydrolyses			Homopolymers obtained		
	$M_w \times 10^{-3}$	$M_n \times 10^{-3}$	I	$M_w \times 10^{-3}$	$M_n \times 10^{-3}$	I
PEA	102	12.1	8.42	115	13	8.84
PPA	98.5	11.2	8.79	110.5	12.3	8.95
PBA	94	9.8	9.59	107	10.98	9.74
PHEA	96.7	10.7	9.03	109	11.6	9.40
PHPA	91	8.3	10.96	103.2	9.23	11.18
PHBA	86	6.8	12.64	97	7.44	13.03

The numerous structural information obtained by the application of such methods will provide suggestions and arguments supporting the topo-chemistry of UV

initiated grafting of wool fibers with alkyl- and hydroalkyl acrylated monomers from homologous series.

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GREFAREA LÂNII PRIN INIŢIERE CU RADIAŢII UV
VII. Analize structurale ale fibrelor de lână grefate cu monomeri alchil şi hidroxialchil acrilaţi

(Rezumat)

Asupra fibrelor de lână românească sort 22 grefate de noi, prin tehnica iniţierii UV, cu monomeri alchil şi hidroxialchil acrilaţi s-au realizat multiple determinări de analiză structurală.

Rezultatele obţinute prin microscopie electronică cu baleiaj efectuate longitudinal şi în fractura fibrelor, prin măsurători de birefringenţă, prin spectroscopie IR şi IR-ATR şi prin determinări de cromatografie în gel permeabil au condus la concluzii importante privind structura fibrelor martor şi modificate.

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Secţia VIII
TEXTILE. PIELĂRIE

THE CRYSTALLINITY DEGREE OF CHEMICALLY MODIFIED FLAX FIBERS, MEASURED BY X-RAY DIFFRACTION

BY

ADRIANA MUSTAŢĂ

The present paper deals with the establishment of the cristallinity index for bleached flax fibers, by X-ray diffraction, under different conditions.

1. Introduction. Flax fibers contain 71-76% cellulose, 13-18% hemicelluloses, pectic and proteic substances, minerals, resins, lignin, tannins, waxes, the amounts of which very depending on the climate and soil conditions, applied agrotechnics, intensity of the fibers extractions from the stems, etc. [1], [2], [3].

The main constituent of the flax fibers, the natural polymer – cellulose – possesses domains of maximum ordering, called crystalline zones, created by the crosslinks between the macromolecules. Such links appear as a result of the interchain attraction forces – the hydrogen links [2], [3]. The ratio between the volume of crystalline zones and the total volume of fibers is called index of crystallinity, a parameter influencing both the chemical polymers – properties and the mechanical fibers characteristics.

The finishing treatments applied to flax aim at a partial removal of flax incrustations which will be reflected in an apparent increase of the crystallinity fibers.

The crystallinity index represents one of the criteria applied in characterizing the finishing treatments efficiency of the flax products.

The present paper deals with the establishment of the crystallinity index for bleached flax fibers, by X-ray diffraction, under different conditions.

2. Experimental. The crystallinity of the chemically – modified flax fibers has been determined by X-ray diffraction. The variants of bleached flax fibers considered for the study are listed in Table 1. In the experiments, fibers extracted from unretted stems belonging to the Hera type (the Joseni area) have been used. Cleaning off their woody parts was one of the effects of crushing and carding operations.

The first stage of the bleaching process – treatment with a solution of hypochlorite or sodium chlorite – was developed at ambient temperature for all variants, although the classical treatment with a sodium chlorite solution takes place at temperatures ranging from 80°C to 90°C.

This variant was preferred for obtaining preliminary data required for the selection of a bleaching technology at ambient temperature, which could be applied for flax.

Table 1

Bleaching variants applied to flax fibers

Stages of bleaching process	Parameters of the bleaching process	Variant				
		V_I	V_{II}	V_{III}	V_{IV}	V_V
1.	Concentration of the sodium hypochlorite solution, [g/L] active chlorine	2 pH=10	2 pH=10	–	–	–
	Concentration of the sodium chlorite solution, [g/L]	–	–	5	4	4
	Temperature of solution, [°C]	23	23	20	20	20
	Duration of action, [min]	100	60	140	180	105
	Rinsing with addition of sodium tripolyphophate, [g/L]	–	–	5	5	5
	Duration, [min]	10	15	5	5	5
	Water temperature, [°C]	20	20	70	70	70
2.	Treatment with sodium sulphite solution:					
	– concentration, [g/L]	7.5	–	6	6	6
	– temperature, [°C]	23	–	20	20	20
	– duration, [min]	30	–	140	105	105
	Rinsing with water at 60°C with addition of sodium tripolyphosphate					
3.	Treatment with hydrogen peroxide 35% solution:					
	– concentration, [mL/L]	90	120	90	90	90
	– boric acid, [mL/L]	–	–	7	5	5
	– trilon B, [g/L]	6	–	–	–	–
	– duration, [hours]	21	1	24	24	24
	– temperature, [°C]	23	72	20	20	20
	Rinsing with water:					
	– temperature, [°C]	50	70	60	60	60
	– duration, [min]	10	10	5	5	5
	– sodium tripolyphosphate, [g/L]	5	5	5	5	5
	– polyglycol, [g/L]	–	–	7	5	5

The hydromodule used in each stage of the bleaching variants (given in Table 1) was of 1:10.

Determination of the fibers crystallinity index was based on planimetering of the diffractograms corresponding to each variant.

X-ray diffraction has been measured on a Kristalloflex 4 – Siemens diffractometer. The radiation bundle (λ=1.54 Å) from the copper anode tube was filtered on a nickel filter, which meant operating through diffraction only with copper's $K\alpha_1$ radiation. The diffraction intensity in pulses/min has been amplified, integrated and recorded by means of a compensograph. The weight of the parallelized bundle fibers exposed to radiations was of 0.3 g. The method of determination through reflexion has been applied, the axes fibers being perpendicular to the goniometer's plane. Other characteristics of the installation are:

– anodic voltage: 35 kV;

– anodic current: 10 mA;

- angular rate of the contour: 2° min;
- rolling rate of the recording paper: 2 cm/min;
- measurement installation error: 2%;
- plot/gap of the X-ray tube: 1°;
- plot/gap of the contour: 1 min.

3. Results and Discussions. The diffractograms obtained have been planimetered between the angles: 2θ=12-28°, as, it is within this interval that both crystalline and amorphous zones are evidenced, while calculation of the crystallinity index has been based on the methodology given in literature [5],...,[8].

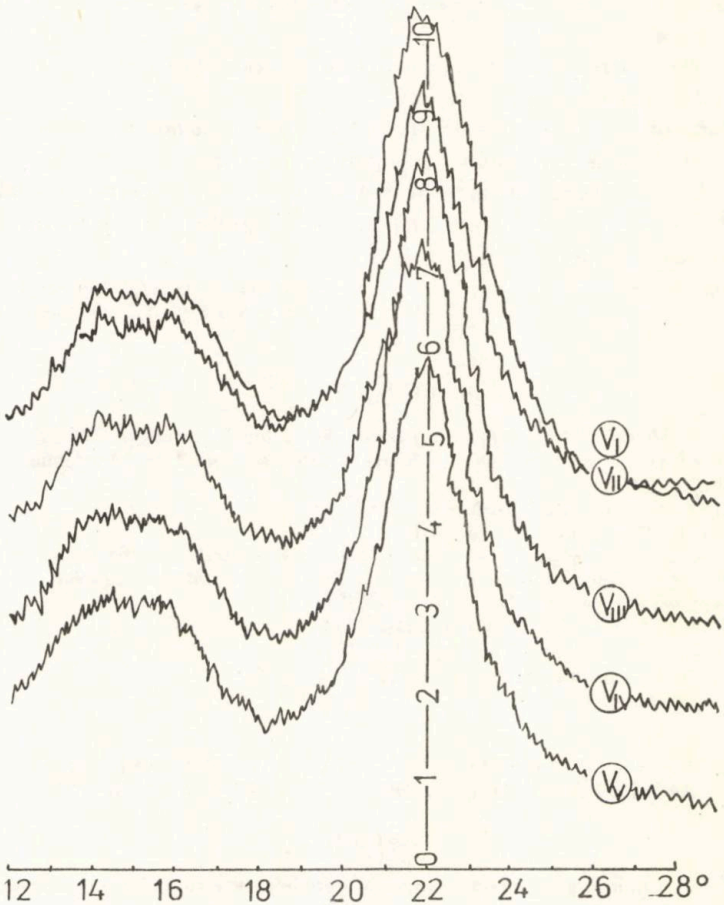

Fig. 1.– Diffractograms of bleached flax fibers.

Analyzing the values of the crystallinity index listed in Table 2, determined by planimetering of the diffractograms plotted in Fig.1, the following ideas may be drawn:

– The same index of crystallinity may be obtained when the first bleaching stage involves treatment with a sodium hypochlorite solution 2 g/L active chlorine for 60

Table 2
Crystallinity index of the bleached flax fibers

Variant	Index of crystallinity, [%]
V_I	52.26
V_{II}	48.68
V_{III}	50.12
V_{IV}	50.31
V_V	47.56

min at 23°C, or treatment with 4 g/L sodium chlorits for 105 min at 20°C. In both cases, treatment with a hydrogen peroxide solution was performed at cold for 24 h, or at 72°C for 60 min.

– For the flax fibers treated chemically in the mentioned variants, the crystallinity index has values ranging from 47 to 52%.

4. Conclusions. 1. The crystallinity index of the bleached flax fibers, in the 5 variants listed in Table 2, evidenced no significant modifications.

2. The chemical treatments applied (see Table 1) do not modify essentially crystallinity of the tested fibers, so that no chemical degration of the textile material under study seems to occur.

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GRADUL DE CRISTALINITATE, MĂSURAT PRIN DIFRACŢIA RAZELOR X, AL FIBRELOR DE IN MODIFICATE CHIMIC

(Rezumat)

Se urmăreşte stabilirea prin difracţia razelor X a gradului de cristalinitate pentru fibrele de in extrase din tulpini netopite şi albite în diferite variante.

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Secţia VIII
TEXTILE. PIELĂRIE

LAQUE POUR LE REVÊTEMENT ANTISTATIQUE

PAR
MARIN DINU, VALERIA NISTOR et GH.-FLORIN DINU

Dans les filatures de laine peignée, à côté de l'avivage et de l'émulsification des fibers, il est nécessaire d'appliquer sur les organes de travail des machines des laques antistatiques.

Dans ce but, on a conçu et expérimenté à l'échelle industrielle une composition ayant des propriétés antistatiques pour le revêtement des composantes des machines textiles, qui viennent en contact avec la matière fibreuse.

L'effet antistatique du film se manifeste envers sous les types de fibres et de leurs mélanges.

1. Introduction. Les fibres textiles, notamment celles synthétiques, ont la tendance de polariser temporairement. La charge à l'électricité statique produit de nombreux effets ayant des conséquences négatives sur le productivité, la qualité des produits et sur la sécurité du travail. Le problème de la neutralisation des charges électriques est d'autant plus important que les derniers temps les fibres synthétiques tendent à prédominer de plus en plus.

Les surfaces métalliques qui viennent en contact avec les textiles en mouvement, la surface des cylindres des bancs d'étirage et des galets de guidage des machines textiles doivent être revêtues d'une laque antistatique pour prévenir la charge électrostatique des fibres, qui peut intervenir comme résultat de leur frottement contre les surfaces respectives dans les processus technologiques.

La charge à électricité statique dans les textiles apparaît parce que:

– le textile a un contenu réduit d'humidité;

– le contact et le frottement sont intensifs;

– la vitesse d'usinage et la pression sur les cylindres supérieurs sont importantes;

– le contenu en substances d'avivage et anti-statiques est réduit;

– l'affinité entre le textile et la matière des organes d'usinage est plus grande (conformément à l'échelle des tensions électrostatiques).

La modification de l'humidité relative de l'air influence parfois la position dans la série de tensions électrostatiques des fibres hydrophiles et de celles synthétiques également.

Le comportement électrostatique des textiles est un peu différent de celui d'autres matières par le fait que pendant l'usinage les fibres d'un mélange polarisent différemment parfois même dans le cadre du même type de fibre (ex. la fibre de polyester). Comme suite de cette caractéristique, les moyens pour la prévention ou la limitation des effets perturbateux des charges électrostatiques doivent être réalises

d'une manière adéquate.

A part l'avivage ou l'émulsionnement des fibres il est nécessaire d'appliquer des laques antistatiques sur les organes de travail qui composent les machines (les manchons en caoutchouc des cylindres supérieurs de pression, les entonnoirs condendeurs des laminoirs, les cylindres des bancs d'étirage des métiers à filer, etc.).

Actuellement on connaît des laques qui s'appliquent sur les surfaces des organes de travail qui composent les machines textiles, mais qui présentent le désavantage de ne pas former des pellicules avec une résistance et adhérence suffisantes, de qui mène a une plus grande fréquence de l'opération de vernissage qui doit être reprise après 24...48 heures de fonctionnement des composantes respectives [1].

Les produits respectifs sont constitués de deux composants (résine et renforçateur) qui se mélangent dans différentes proportions avant l'application.

Parmi les laques utilisées plus fréquemment dans la pratique industrielle, on peut citer:

a) Laque pour les manchons en caoutchouc de la filature [2], qui consiste d'une première solution contenant 1 partie d'oxyde chromique et 2...3 parties de laque alkydo-aminique, qui se mélangent en proportion de 1:0,005 avec une autre solution formée d'une partie HCl 32% et 4 parties éthanol 94%. Ce produit présente le désavantage de ne pas pouvoir être utilisé dans les filatures de laine 100%, de PAN 100% ou PAN en mélange avec des fibres chimiques.

b) Laque pour manchons en caoutchouc de la filature [3], formée d'une première solution constituée d'une partie (en poids) d'oxyde noir de fer, trois parties (en poids) de laque aminique (qui contient comme liant de la résine uréoformaldéhydique éterifiée et 1 g/l de produit antistatique) et une deuxième solution acide ayant 7,2% acide. Du moment de l'application, la première solution se mélange avec la deuxième en rapport (gravimétrique) de 1:0,1. Ce produit, tout comme le premier, présente le désavantage d'une adhérence insuffisante aux surfaces sur lesquelles on l'applique, en s'exfoliant après environ 2...3 jours et à l'application il pollue l'espace où on l'utilise.

2. Partie expérimentale. Pour éliminer les désavantages présentés ci-dessus on a conçu et expérimenté industriellement une composition ayant des propriétés antistatiques pour le revêtement des composantes des machines textiles qui viennent en contact avec la matière fibreuse, constituée de: 50-70% polyéthylène-éthène isocyanate, 30-50% clorure de méthylène, 0,05-0,5% polyéthylèneglycole, le polyéthylène-éthène-isocyanate ayant une masse moléculaire entre 800 et 4000, un contenuu de doubles liaisons réactives de 0,5-8 moles/mol et une concentration de groupes NCO de 2-6 moles/mol [4].

Les composants de la recette se mélangent en agitant, à la température ambiante, l'agitation continuant encore 20-30 minutes; après, le produit peut être appliqué.

La composition mentionnée ci-dessus constitue un seul produit qui s'applique en couche sur la surface polie et dégraissée conformément aux procédés usuels de vernissage. Sur les surfaces métalliques on l'applique sans phosphatage préalable. La pellicule réalisée sèche à la température ambiante ou à des températures au-dessous de 100°C, lorsqu'on a comme but la diminution de la durée de séchage. La pellicule est élastique, ayant une trés bonne adhérence et une résistance agrandie aux solvents,

huiles et produits d'avivage, elle résiste longtemps sur les surfaces appliquées, en se détruisant avec le temps, comme suite des frottements accentués.

Ce produit présent les avantages suivants:

a) La laque constitue un seul produit qui s'applique directement sans nécessiter le mélange de la résine avec le renforçateur comme on le fait pour les laques connues jusqu'à présent;

b) On l'obtient facilement et présente de la stabilité dans le temps;

c) La pellicule formée sur les surfaces appliquées a une grande adhérence et présente une bonne résistance au choc et aux agents chimiques;

d) Parce qu'elle ne s'exfolie pas, la pellicule résiste sur le surface appliquée une longue période de temps;

e) L'effet anti-statique de la pellicule se manifeste envers tous les types de fibres et leurs mélanges;

f) La laque adhère trés bien tant aux métaux qu'aux caoutchoucs nitriliques dont on fabrique les manchons des cylindres des bancs d'étirage.

3. Conclusions. L'emploi de la laque anti-statique qui fait l'objet de ce travail détermine les avantages suivants:

- on réduit beaucoup la charge électrostatique des matières usinées;
- la laque résiste longtemps sur les surfaces appliquées;
- la laque se prête à tous les types de fibres et à leurs mélanges.

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LAC PENTRU ACOPERIREA ANTISTATICĂ A COMPONENTELOR MAŞINILOR TEXTILE

(Rezumat)

În filaturile de lână pieptănată, pe lângă avivarea şi emulsionarea fibrelor, se impune aplicarea pe organele de lucru din componenţa maşinilor a unor lucruri antistatice. În acest scop s-a conceput şi experimentat industrial o compoziţie cu proprietăţi antistatice pentru acoperirea componentelor maşinilor textile, care vin în contact cu materialul fibros.

Efectul antistatic al peliculei se manifestă faţă de toate tipurile de fibre şi amestecurile acestora.

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MODELAGE MATHEMATIQUE DU PROCESSUS D'USINAGE DES DECHETS TEXTILES INDUSTRIELS UTILISANT L'AGREGAT LAROCHE

PAR

MARIA ZAMFIR, PAUL KIEKENS et LIEVEN VANGHELUWE

Dans cet article sont présentés des éléments de modelage mathématique du processus d'usinage des déchets textiles industriels de tricot, utilisant l'agrégat de coupage-effilochage LAROCHE type OLYMP (France).

Les modèles mathématiques obtenus pour le pourcentage de fibres recyclées, de fils et de tricot noneffilochés en fonction de paramètres technologiques nous aident d'établir leurs valeurs optimales de mise en oeuvre au but d'un rendement maximum.

1. Introduction. L'industrie de nontissés et celle de fils cardés type laine sont les plus grandes consommatrices de fibres recyclées de déchets textiles industriels type acrylique qui résultent du processus de façonnage-confection des détails de tricotage pour des vêtements.

Ces fibres recyclées sont destinées pour des nontissés comme matériaux isolants acoustiques et thermiques, des feutres aiguilletés, des filtres de drainages et parfois des épaulettes dans l'industrie de confection [1], [4].

Les installations modernes d'usinage des déchets textiles par coupage-effilochage, comme par exemple type RORA, ROLANDO, DELL'ORCO & VILLANI (Italie), AUTEFA, SCHIRP (Allemagne), PIERRET (France) et autres permettent d'obtenir des fibres recyclées d'une longueur maximale de 120 mm, correspondant aux destinations ci-dessus. Aussi, ces installations présentent des systèmes spéciaux avec une haute productivité et rendement. Les fibres obtenues sont de qualité. Principalement, avec un système complète elles commencent avec des ballots de déchets textiles jusqu'aux ballots d'effilochure [2], [5], [8].

L'un de ces agrégats le plus connu est LAROCHE type OLIMP (France).

Les principaux éléments de cet agrégat sont:

- machine à couper verticale des ballots de déchets;
- deux machines à couper rotatives des déchets;
- ventilateur de transport des morceaux de déchets coupées à un condensateur;
- depôt de réserve-chargeur de grande capacité;
- effilocheuse avec plusieurs rouleaux d'effilochage;
- système de réalimentation des déchets noneffilochés;
- machine à presser de l'effilochure en ballots.

Le processus d'usinage des déchets textiles par coupage-effilochage peut être caractérisé par la longueur des fibres recyclées, mais surtout par le pourcentage de fibres recyclées, comparé avec le pourcentage de fils et de tricot noneffilochés qui se trouvent dans l'effilochure.

Le but de cet article est de présenter une étude effectuée à l'agrégat LAROCHE type OLIMP pour établir les paramètres optimaux d'usinage par coupage-effilochage des déchtes industriels. Des méthodes de programmation factoriale et de régression ont été utilisées.

2. Experimentations

2.1. L'établissement et l'interprétation statistique des modèles mathématiques. L'étude a été effectuée utilisant un mélange de 100% déchets de tricot type polyacrylonitril de plusieurs couleurs.

Un programme composé, central, rotatif avec deux variables indépendantes a été utilisé pour effectuer les expérimentations. Les deux variables indépendantes proposées pour l'analyse sont:

– la vitesse d'alimentation des morceaux aux machines à couper rotatives, notée x_1;

– la vitesse d'alimentation des petits morceaux après le coupage rotatif dans la machine à effilocher, notée x_2.

Treize expérimentations aléatoires avec une programmation factoriale [3], [6], [7] ont été effectuées, pour lesquelles les valeurs codifiées et réelles des variables indépendantes sont présentées dans le Tableau 1. On peut voir qu'il y a des expérimentations factoriales notées *1* à *4*, extérieures notées *5* à *8* et centrales notées *9* à *13*.

Tableau 1

Programme factorial. Valeurs des variables indépendantes.

Expérimentation	Codifieés		Réelles (m/min)	
	x_1	x_2	x_1	x_2
1	−1	−1	7,08	3,0
2	1	−1	11,32	3,0
3	−1	1	7,08	6,0
4	1	1	11,32	6,0
5	−1,414	0	6,2	4,5
6	+1,414	0	12,2	4,5
7	0	−1,414	9,2	2,4
8	0	+1,414	9,2	6,6
9 à 13	0	0	9,2	4,5

Les paramètres invariables sont:

– la vitesse rotative des trois rouleaux, 630 tours/min;

– le nombre de clous de chaque rouleau à 34 plaquettes (59 000 pour le I-er, 90 000 pour le II-ème et 104 000 pour le III-ème);

– la vitesse rotative des deux couteaux rotatifs, 2 000 tours/min.

Trois variables dépendantes ont été considerées pour le modelage mathématique du processus d'usinage à l'agrégat LAROCHE:

– Y_f, le pourcentage de poids de fibres recyclées;

– Y_F, le pourcentage de poids de fils noneffilochés;
– Y_T, le pourcentage de poids de tricot noneffiloché.

Le modèle mathématique théorique qui a été adopté est un polinom de deux niveaux et deux inconnues [3], [6] d'une forme générale:

$$Y = b_0 + b_1x_1 + b_2x_2 + b_{11}x_1^2 + b_{22}x_2^2 + b_{12}x_1x_2, \tag{1}$$

où: $b_0, b_1, b_2, b_{11}, b_{22}$ et b_{12} représentent les coefficients de régression, calculés après des méthodes mathématiques [6]; x_1 et x_2 représentent les variables indépendantes considerées ci-dessus, en valeurs codifiées; Y représentent les variables dépendantes à analyser.

Les variables dépendantes ont été déterminées par échantillonage d'une masse de 5 gramme des 20 échantillons d'effilochure pour chaque expérimentation, triage en fibres recyclées, fils et tricot nonefillochés, pesage des trois composants utilisant une balance et l'expression en pour-cent du chaque composant.

Les valeurs moyennes des variables dépendantes mesurées sont présentées dans le Tableau 2.

Tableau 2
Valeurs des variables dépendantes et déviations A (%)

Experimentation	Valeurs expérimentales (%)			A (%)	
	Y_f	Y_F	Y_T	Y_f	Y_F
1	34,046	62,300	3,654	11,265	5,166
2	33,678	62,846	3,476	14,821	6,623
3	44,534	54,034	1,432	4,347	1,190
4	43,994	53,232	2,744	1,381	0,565
5	38,998	57,500	3,502	1,798	1,864
6	41,870	54,648	3,482	5,872	4,406
7	44,686	53,986	1,328	12,536	8,283
8	43,316	52,266	4,418	5,627	1,890
9	49,140	49,114	1,746	0,036	0,007
10	48,995	49,204	1,801	0,332	0,175
11	49,179	49,100	1,721	0,043	0,035
12	49,268	49,000	1,732	0,223	0,240
13	49,156	49,104	1,740	0,003	0,027

Le processus d'usinage des déchets est décrit par les modèles mathématiques (2), (3) et (4):

$$Y_f = 49,158 + 0,394x_1 + 2,358x_2 - 5,153x_1^2 - 3,37x_2^2 - 0,043x_1x_2, \tag{2}$$

$$Y_F = 49,118 - 0,536x_1 - 2,539x_2 + 4,35x_1^2 + 2,876x_2^2 - 0,337x_1x_2, \tag{3}$$

$$Y_T = 1,749 + 0,138x_1 + 0,177x_2 + 0,782x_1^2 + 0,473x_2^2 + 0,373x_1x_2, \tag{4}$$

Les modèles mathémathiques (2) et (3) ont été validés par les déviations A exprimées en pour-cent entre les valeurs calculées et celles mesurées des variables dépendantes de moins que 10% (Tableau 2).

Les coefficients de régression b_0, b_1, b_{11}, b_{22} et b_{12} ont été testés par Test Student, la statistique t. Les valeurs calculées t_c sont présentées dans le Tableau 3, où est aussi

Tableau 3
Le testage des coefficients de régression

Coefficients de régression	Test Student calculé (t_c)			Valeur de Student théorique
	Y_f	Y_F	Y_T	
b_0	1114,675	1518,291	125,847	
b_1	11,304	−20,961	12,581	α=0,05
b_2	67,643	−99,276	16,103	υ=4
b_{11}	−137,813	158,564	66,395	
b_{22}	−90,133	104,846	40,136	t_{tab}=2,132
b_{12}	−0,872	−9,317	23,976	

marquée la valeur théorique $t_{\text{tab}} = 2,132$ pour un niveau de signifiance $\alpha = 0,05$ et $\upsilon = 4$ degrés de liberté [6], [7]. Cette valeur théorique sera utilisée pour le testage.

On considère un coefficient de régression significatif, si la rélation $|t_c| \geq t_{\text{tab}}$ est établie.

En conclusion, on peut constater utilisant les données du Tableau 3, que tous les coefficients de régression sont significatifs sauf le coefficient b_{12} pour la variable dépendante Y_f. Ce coefficient a été gardé seulement pour l'analyse statistique, pas pour l'interprétation technologique.

Le pourcentage de fibres recyclées Y_f augmente quand les vitesses d'alimentation aux machines à couper rotatives x_1 et effilocheuse x_2 augmentent aussi.

La vitesse d'alimentation à l'effilocheuse x_2 a une influence par le coefficient de I-er degré de 5,98 (2,358/0,394) fois la vitesse d'alimentation x_1 aux machines à couper.

Le coefficient de II-ème degré b_{11} de la variable x_1 a une influence de 1,52 (5,153/3,37) fois le coefficient b_{22} de la variable x_2.

L'influence est changée par rapport avec les coefficients de régression de II-ème degré.

Le pourcentage de fils noneffilochés Y_F décroit alors que les vitesses d'alimentation aux machines à couper et effilocheuse augmentent. Cela est exprimée par les coefficients de II-ème degré d'influence positive.

Le terme mixte x_1x_2, qui signifie l'interdépendance entre les variables indépendantes, influence normalement la valeur du pourcentage de fils noneffilochés Y_F, fortement le pourcentage de tricot noneffiloché Y_T et n'influence pas le pourcentage de fibres recyclées Y_f.

Le terme mixt x_1x_2 par sa valeur positive montre la tendance d'augmentation du pourcentage de tricot noneffiloché Y_T, à cause de l'action cumulée de ces deux variables indépendantes.

Les variables indépendantes considérées influencent significativement, directement et positivement le pourcentage de tricot noneffiloché.

Si on analyse intégralement les trois variables dépendantes Y_f, Y_F et Y_T, exprimées par les modèles mathématiques (2), (3) et (4) on peut constater que l'action cumulée des variables indépendantes x_1 et x_2 détermine l'augmentation de pourcentage de tricot noneffiloché Y_T, réplique de même intensité (-0,337) le décroissement du pourcentage de fils noneffilochés Y_F, mais n'influence pas le pourcentage de fibres

recyclées Y_f.

L'influence des variables indépendantes peut être aussi mise en évidence, par les coefficients de corrélation multiple qui ont les suivantes valeurs:

$$R_{Y_f \cdot x_1,x_2} = 0,8731, \quad R_{Y_F \cdot x_1,x_2} = 0,8945 \quad \text{et} \quad R_{Y_T \cdot x_1,x_2} = 0,6819.$$

Ces valeurs sont hautes, si on considère que des déchets textiles ont été utilisés.

Aussi, ces valeurs ont été validées utilisant le Test Fischer-Snedecor, la statistique F d'une valeur théorique F_{tab}=4,1 [6], [7] pour un niveau de signifiance α=0,05 et des degrés de liberté v_1=2 et v_2=10.

Les valeurs calculées de la statistique F sont: 16,035 pour Y_f, 20,023 pour Y_F et 4,343 pour Y_T. Donc, elles sont plus hautes que la valeur de 4,1 et les valeurs des coefficients de corrélation multiple sont validées.

Le coefficient de détermination multiple a été calculé pour le pourcentage de fibres recyclées et il a la valeur:

$$d_{Y_f \cdot x_1,x_2} = R^2_{Y_f \cdot x_1,x_2} = 0,7623.$$

Cette valeur nous montre que le pourcentage de fibres recyclées est influencé en proportion de 76,23% par les variables indépendantes x_1 et x_2.

Donc, il y a d'autres facteurs qui en proportion de 23,77% ont une influence noncontrolée dans le processus de coupage-effilochage des déchets textiles.

On peut noter les facteurs suivants: le processus d'avivage sur les déchets, le degré d'usure aux couteaux rotatifs et clous d'effilocheuse, l'hétérogènéité des déchets de tricot (l'épaisseur, le titre des fils, l'armure, le finissage en couleurs claires ou foncées, etc.).

2.2. L'interprétation technologique des modèles mathématiques. Les modèles mathématiques de la dépendance du pourcentage de fibres recyclées Y_f, de fils Y_F et de tricot noneffilochés Y_T, en fonction de paramètres du processus d'usinage des déchets textiles utilisant l'agrégat LAROCHE type OLYMP (France) sont présentés dans les Figs.1, 2 et 3.

Les modèles mathématiques (2), (3) et (4) décrivent:

– un volume parabolique ellipsoïdal avec un point maximal pour le pourcentage de fibres recyclées (Fig.1*a*);

– des volums paraboliques ellipsoïdals avec des points minimaux pour le pourcentage de fils noneffilochés (Fig.2*a*) et de tricot noneffiloché (Fig.3*a*).

Ainsi, on peut noter les idées suivantes:

– les surfaces de réponse (coupes horizontales) sont elliptiques et elles traversent le domaine expérimental (Figs.1*c*, 2*c* et 3*c*);

– les points stationaires, de maximum ou de minimum se trouvent tout près du centre d'expérimentation.

Dans le plan des courbes de niveau constant, le pourcentage de fibres recyclées Y_f est représenté par les courbes y_1 à y_5 de valeurs: 49,268%, 48,995%, 44,686%, 43,994% et 41,87%.

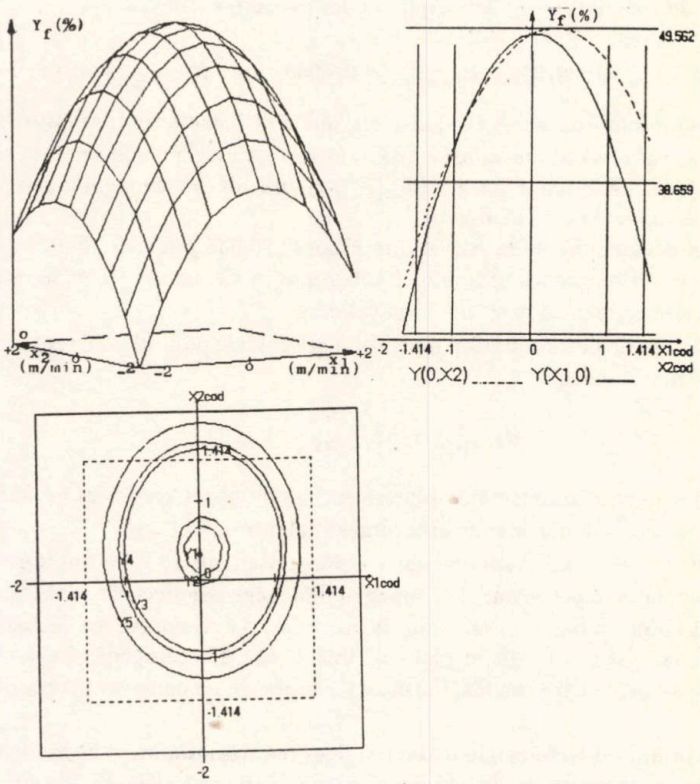

Fig. 1.– Variation du pourcentage de fibres recyclées (Y_f) à l'agrégat LAROCHE.

Une valeur maximale de fibres recyclées de 49,578% est à réaliser aux valeurs suivantes des variables indépendantes: x_1=0,038 et x_2=0,35 codifiées, correspondant les valeurs réelles x_1=9,28 m/min. et x_2=5,02 m/min.

La valeur de 49,578% de fibres recyclées qui est le point de maximum pour le modèle (2) représente en réalité un point optimal technologique dans les conditions données.

Le pourcentage de fils noneffilochés Y_F est repreésenté dans le domaine expérimentale par les courbes y_1 à y_5 de valeurs: 49,0%, 52,266%, 53,232%, 57,5% et des portions pour 62,3%.

Une valeur minimale de fils noneffilochés se réalise utilisant les suivants paramètres: x_1=0,079 et x_2=0,446 codifiés, correspondant les valeurs réelles x_1=9,367 m/min. et x_2=5,169 m/min.

Le pourcentage de tricot noneffiloché Y_T est aussi présenté dans le domaine

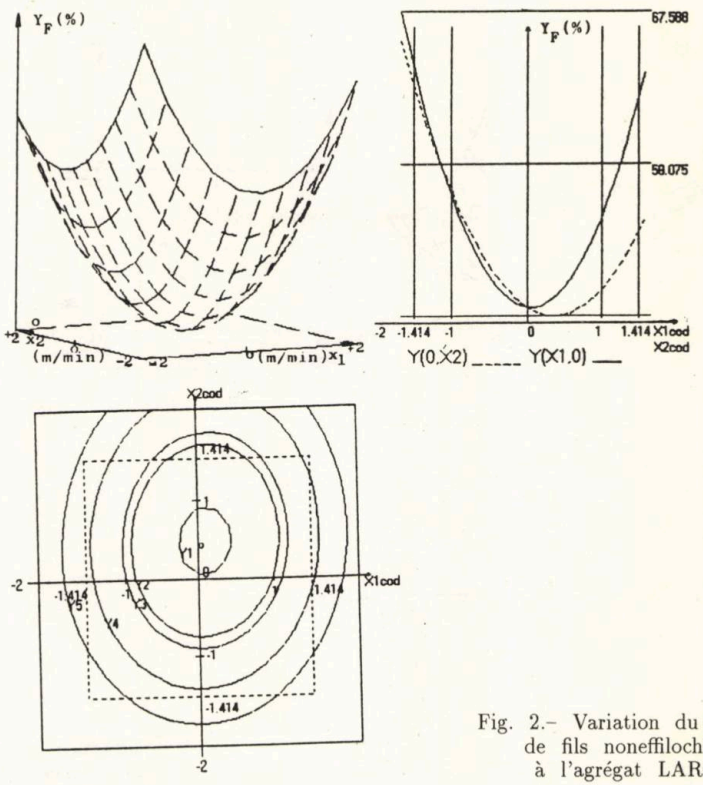

Fig. 2.– Variation du pourcentage de fils noneffilochés (Y_F) à l'agrégat LAROCHE.

expérimental par les courbes y_1 à y_4 de valeurs 1,74%, 1,801% et 3,482%. Tout près de domaine expérimental traverse la courbe y_4=4,418%.

La valeur minimale de tricot noneffiloché, le point de minimum du modèle (4) représente en réalité un point optimal technologique. Il a la valeur de 1,731% et se réalise utilisant les paramètres: x_1=–0,048 et x_2=–0,168 codifiés, en valeurs réelles x_1=9,30 m/min. et x_2=4,752 m/min.

L'influence de chaque variable indépendante, séparée et individuelle quand une autre prend la valeur centrale du domaine expérimental (x_1=0, respective x_2=0, codifiées) est représentée dans les Figs.1*b*, 2*b* et 3*b*.

On peut soulignier les idées:

– Pour les valeurs des variables indépendantes situées à gauche du centre d'expérimentation (–1,414 ... 0) codifiées, le pourcentage de fibres recyclées augmente jusqu'à une valeur maximale située tout près du centre d'expérimentation; mais à l'autre coté le pourcentage de fils et de tricot noneffilochés décroissent jusqu'aux valeurs minimales, aussi tout près de centre d'expérimentation;

– Pour les valeurs aux variables indépendantes situées à droit du centre d'expérimentation (0,...,+1,414) codifiées la variation des variables dépendantes

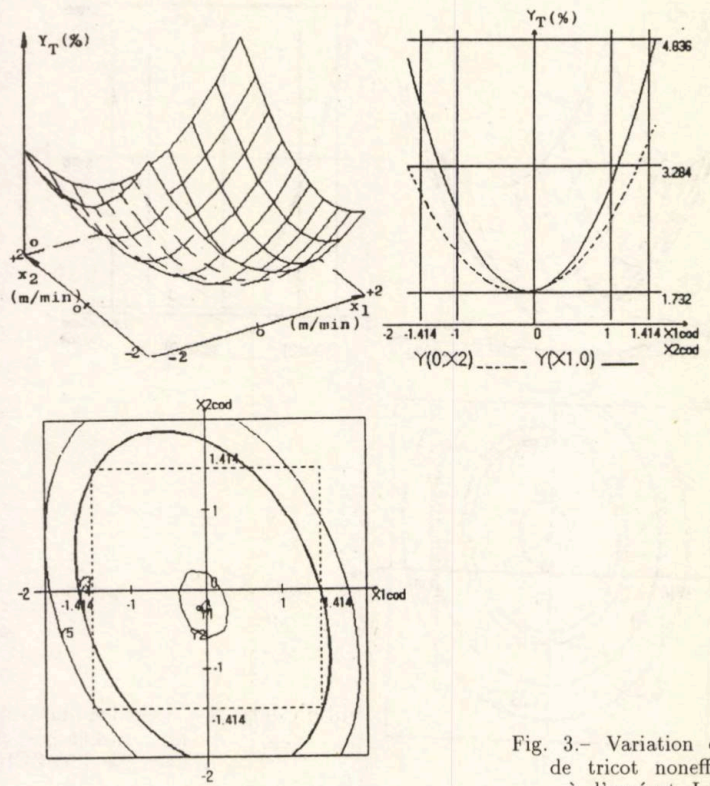

Fig. 3.– Variation du pourcentage de tricot noneffiloché (Y_T) à l'agrégat LAROCHE.

s'inversent d'une symètrie presque parfaite par rapport au centre du domaine expérimental.

3. Conclusions. À la fin de cette étude on peut soulignier les idées suivantes:

– Les points stationnaires de maximum ou de minimum obtenus pour les modèles mathématiques du pourcentage de fibres recyclées, de fils et de tricot noneffilochés représentent des points optimals technologiques en réalité.

Ainsi, on peut dire que l'étude est correctement effectué, parce que pour un pourcentage maximal de fibres recyclées a été obtenu un pourcentage minimal de fils ou de tricot noneffilochés;

– Le pourcentage maximal de fibres recyclées dans un processus d'usinage des déchets textiles de tricot utilisant l'agrégat LAROCHE on peut réaliser aux suivants paramètres technologiques: $x_1 \in (-0,5,...,+0,5)$ codifié, $x_1 \in (8,14,...,10,26)$ m/min en réalité et $x_2 \in (-0,5,...,+0,5)$ codifié, $x_2 \in (3,75,...,5,25)$ m/min. en réalité;

– Le pourcentage minimal de fils ou de tricot noneffilochés on peut réaliser aux même paramètres que ci-dessus;

– Le processus d'usinage des déchets textiles industriels par coupage-effilochage

peut être modelé mathémathiquement, utilisant des méthodes de programmation factoriale et de régression qu'ont pour but d'établir les valeurs optimales pour les paramètres technologique de mise en oeuvre;

– Les auteurs de cet article peuvent soulignier qu'encore autres paramètres technologiques du processus par coupage-effilochage sont importants, comme par exemple la densité de clous des rouleaux d'effilochage, l'angle d'inclination des clous, les vitesses des couteaux rotatifs et des rouleaux d'effilochage. Mais, ces paramètres doivent d'avoir cinq niveaux de variation correspondant à la programmation factoriale et donc ils peuvent être modifiés seulement par le fabricant d'agrégat.

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MODELAREA MATEMATICĂ A PROCESULUI DE PRELUCRARE A MATERIALELOR TEXTILE REFOLOSIBILE TEHNOLOGICE UTILIZÂND AGREGATUL LAROCHE

(Rezumat)

Sunt prezentate elemente de modelare matematică a procesului de prelucrare a materialelor textile refolosibile tehnologice rezultate de la croire-confecţionare a detaliilor de îmbrăcăminte din tricoturi.

Modelele matematice obţinute, pentru procentul de fibre recuperate, procentul de fire nedefibrate şi procentul de bucăţi de tricot nedestrămate exprimate în funcţie de parametrii tehnologici, permit optimizarea procesului tehnologic de la agregatul LAROCHE.

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ÉTUDE DE LA STABILITÉ THERMIQUE DES SUBSTANCES D'ENCOLLAGE

PAR
M. CIOCOIU

L'ouvrage present létude de la stabilité thermique des substances d'encollage utilisant l'analyse thermique differentielle où a effectué des recherches sur les substances MEDACRIL ST, ARACET APV, GEROL ACR et VINAROL ST.

1. Introduction. Pendant le fonctionnement de l'appareil à encoller surviennent des situations ou la vitesse de celui-ci doit être réduite ou des situations ou l'appareil doit être arrêté à la suite des avaries, les fils qui se trouvent dans le séchoir étant soumis alors à des températures élevées pendant une période bien plus longue qu'il n'est important de connaître la façon dont réagit l'adésif utilisé dans le procédé d'encollage à des températures élevées, du point de vue de sa stabilité chimique.

A ce sujet, on ne trouve, dans la littérature de spécialité, que les articles de J. T r a u t e r [1],...,[3].

Nos recherches ont utilisé l'analyse thermique différentielle (DTA) ou la spectroscopie thermique, qui consiste à mesurer les effets thermiques qui accompagnent le réchauffement ou, selon le cas, le refroidissement de la substance étudiée.

2. Expérimentations propres. On réchauffe la substance d'encollage en même temps qu'un échantillon inerte (γ-Al_2O_3) à une vitesse constante et on détermine leur gradient de temperature en fonction de la température et du temps écoulé. La dépendance indiquée, exprimée par les courbes enregistrées, appelées thermogrammes ou spectres thermique, donne la possibilité de déterminer la température, la chaleur, la perte de poids et la vitese de réalisation de ces états, en mettant donc en évidence, s'il y a lieu, l'existence de reactions exo et endothermiques.

Les essais ont été effectués sur un dérivatographe MOM du type 102; pour chaque thermogramme on a enregistré automatiquement les quatres courbes suivantes:

– la courbe T, qui indique l'augmentation de la température de l'échantillon, mesurée dans le creuset;

– la courbe TG, qui indique la perte de poids pendant le réchauffement;

– la courbe DTG, qui indique la vitesse de la perte de poids;

– la courbe DTA, qui indique la catégorie des effects thermiques qui accompagnent les transformations physiques et chimiques respectives.

Les conditions de travail ont été les suivantes:

– le poids des échantillons: 30 mg, 50 mg;

– la vitese de réchauffement: 4°C/min. pour les essais jusqu'à 100°C; 6°C/min. pour les essais jusqu'à 150°C;

– de petits creusets à couvercle;

– un régime dynamique (avec évacuation de gaz);

– les sensibilités: T:150°C; TG:20 mg; DTG:1/15; DTA:1/15;

– les échantillons ont été apportés à l'état de poudre avec de l'aluminone (γ-AL_2O_3).

On à effectué des recherches sur les substances MEDACRIL ST, GEROL ACR, VINAROL ST, ARACET APV, les courbes obtenues étant présentées dans les Figs. 1,...,4.

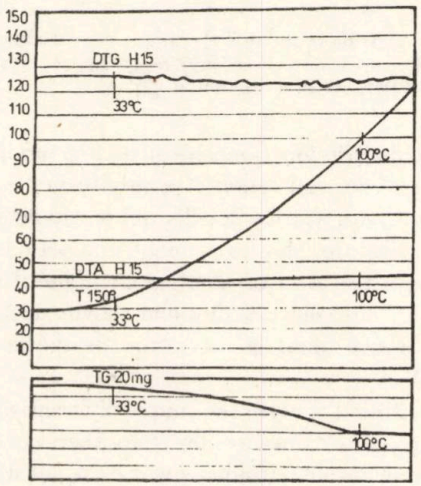

Fig. 1.– Thermogramme MEDACRIL.

2.1. Étude comparative du produit roumain MEDACRIL et du produit d'importation GEROL. En analysant les courbes des Figs.1 et 2 on observe que leurs allures sont semblables, ce qui montre un comportement identique des deux produits. Pour le MEDACRIL ainsi que pour le GEROL la température maximale obtenue à été de 120°C; il y a donc un gradient de vitese d'approximativement 5°C/min par rapport à 6°C/min qui était prévu, ce qui prouve une conductibilité thermique réduite.

Comme on peut le voir au Tableau 1, les pertes de poids des deux substances sont pratiquement identiques et ce n'est que la façon dont le poids se modifie qui diffère (la ligne DTG par rapport à la ligne TG). C'est ainsi que dans la zone de température qui nous intéresse, la zone qui va jusqu'à 100°C et surtout la zone située entre 100°C et 120°C, les pertes de poids sont identiques pour les deux produits étudiés. On ne remarque pas, dans la zone de température observée, des phénomènes endothermiques importants, la descente sous l'horizontale de la ligne DTA est due

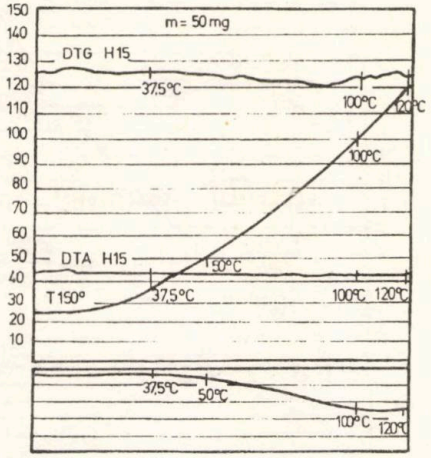

Fig. 2.– Thermogramme GEROL.

au phénomène de perte de poids par l'élimination de l'eau et des substances volatiles.

Tableau 1

N°.	Intervalle de température [°C]	Vinatrol ST		Aracet APV	
		Perdition de masse		Perdition de masse	
		mg	%	mg	%
1	37,5-50	0,20	0,40	0,42	0,84
2	50-100	1,74	3,40	1,80	3,60
3	100-120	0,30	0,60	0,30	0,60

Nous pouvons donc montrer que:

– le produit roumain MEDACRIL est tout à fait similaire au produit GEROL de ce point de vue;

– lors d'un stationnement prolongé à des températures comparables à celles de la zone de contact du fil sur le cylindre de séchage, la pélicule ne se dégrade pas.

2.2. Étude comparative du produit roumain ARACET APV et du produit d'importation VINAROL ST. En analysant les courbes des Figs.3 et 4 on observe que leurs allures sont semblables, ce qui démontre un comportement identique des deux produits vis-à-vis du test respectif.

Pour ces produits la température de réchauffement maximale à été de 150°C, température prĕvue; ces produits sont donc de meilleurs conducteurs de chaleur que les produits constitués surtout d'acrylates.

Comme on peut le voir au Tableau 2 les pertes de poids sont semblables pour l'ARACET et pour le VINAROL jusqu'à 110°C, c'est-à-dire dans le domaine qui nous intéresse.

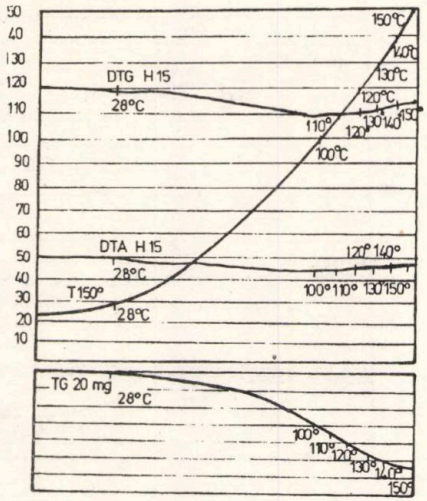

Fig. 3.– Thermogramme VINAROL.

Tableau 2

N°.	Intervalle de température [°C]	Vinatrol ST		Aracet APV	
		Perdition de masse		Perdition de masse	
		mg	%	mg	%
1	28-100	2,78	5,50	2,50	5,00
2	100-110	0,62	1,24	0,58	1,10
3	110-120	0,50	1,00	0,44	0,88
4	120-130	0,50	1,00	0,28	0,56
5	130-140	0,38	0,76	0,18	0,36
6	140-150	0,25	0,50	0,12	0,24

Jusqu'à 100°C la pellicule d'ARACET présente une perte de poids de 3,54 mg, et celle de VINAROL de 3,40 mg. Pour la zone allant 110°C à 150°C les pertes de poids sont plus importantes pour VINAROL: dans la zone allant de 110°C à 150°C la pellicule de VINAROL souffre des pertes 2,5 fois plus grandes que dans la zone qui va jusqu'à 110°C, tandis que la pellicule d'ARACET présente des pertes seulement 1,5 fois plus grandes. Cela démontre une meilleure stabilité thermique de la pellicule d'ARACET. La courbe DTA évolue semblablement pour les deux produits; à la température de 120°C (probablement température maximale utilisée pour sécher les fils de viscose), la courbe présente un point d'inflexion justement sur la ligne de référence.

De toute façon, les processus endo- et exothermiques indiqués par la courbe ont une intensité réduite et n'affectent pas les qualités de la pellicule.

Par conséquent, on peut montrer que:

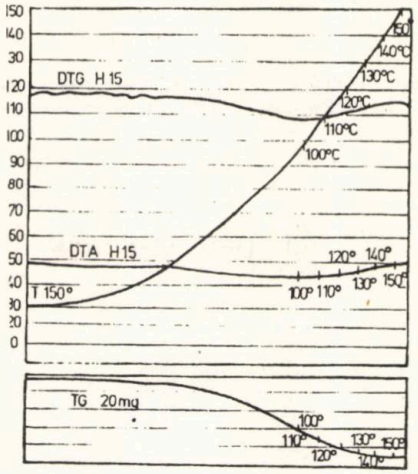

Fig. 4.– Thermogramme ARACET.

– le produit roumain ARACET est similaire au produit d'importation VINAROL;

– la stabilité thermique du produit ARACET est plus grande dans le domaine dangereux, au-dessus de 110°C, que celle du produit d'importation, ce qui recommande le produit roumain pour être utilisé dans le processus d'encollage.

3. Conclusions

a) La stabilité thermique du produit roumain MEDACRIL est similaire à celle du produit d'importation GEROL.

b) La stabilité thermique du produit roumain ARACET est meilleure, dans la domaine critique (de 100° à 120°C), que celle du produit d'importation VINAROL.

c) Le stationnement accidentel de fils dans le séchoir pendant une période prolongée n'a pas d'influence négative sur la qualité de la pellicule, ni donc sur la qualité des fils encollés.

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STUDIUL STABILITĂŢII TERMICE A SUBSTANŢELOR DE ÎNCLEIERE

(Rezumat)

Se prezintă un studiu în DTA a substanţelor de încleiere româneşti prin comparaţie cu cele din import. Cercetările pun în evidenţă similitudinile şi deosebirile între substanţele respective.

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CONTRIBUTIONS À LA RECHERCHE DE LA VISCOSITÉ DE L'APPRÊT POUR L'ENCOLLAGE À BASE D'AMIDON AVEC SCINDEMENT PAR CAVITATION HYDROACOUSTIQUE

PAR
DANIELA LIUŢE et P. DUMITRAŞ

Les apprêts pour l'encollage des chaînes à base d'amidon sont préparés par différénts procédés technologiques qui poursuivent la diminution des dimensions des grains par scindement et l'obtention d'une solution colloïdale homogène. L'homogénéité des solutions et le degré de scindement sont fortement influencés par le principe technologique employé à la preparation de l'apprêt pour encollage.

1. Étude de certaines caractéristiques de thixotropie. L'apprêt pour l'encollage à base d'amidon est un fluide non-newtonien aux caractéristiques thixotropes, auquel entre la viscosité et la tension de cisaillement il y a la relation suivante:

$$\tau = \eta \dot{\gamma}_n$$

où $\dot{\gamma} = \mathrm{d}v/\mathrm{d}x$ représente le gradient de la vitesse de cisaillement et le coefficient exponentiel $\eta \neq 1$.

La tension de cisaillement a été mesureé à l'aide de rheóviscosimètre à cylindres coaxiaux type Rheothest (diagramme nr.1) à base de la relation spécifique pour l'appareil: $\tau = z\alpha$ où z représente la constante de cylindres utilisés et α représente la valeur de la gradation sur l'échelle de mesurage du moment de rotation du dynamomètre compris dans la structure de l'appareil.

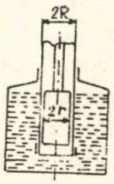

Fig. 1

À partir des caractéristiques techniques de l'appareil „Rheothest 2" (Fig.1) et de la méthode de travail spécifique pour celui-ci, pour la détermination de la viscosité on a choisi le cylindre de mesurage S2 auquel correspond les caractéristiques suivantes:

– le rapport entre le rayon extérieur du cylindre central r et le rayon intérieur du cylindre tubulaire extérieur R est r/R=0.94;

– la tension de cisaillement pour première region de mesurage τ=30...600 dyn/cm^2 et pour la deuxième region τ=300...600 dyn/cm^2;

– le gradient de la vitesse de cisaillement $\dot{\gamma}$=0,5...437 rad/s;

– le domaine de mesurement de la viscosité η=7...120000 cP pour la première region et η=70...1 200 000 cP pour la deuxième region.

Le gradient de la vitesse de cisaillement correspondant à la frequence de 50 Hz

et au cylindre de mesurage utilisé a eu les valeurs 1; 1,8; 3; 5,4; 9; 16,2; 27; 48,6; 81; 145,8; 243; 437,4.

Si la frequence du circuit de mesurage est différente de 50 Hz on corrigera $\dot{\gamma}$ avec la relation:

$$\dot{\gamma}_c = \dot{\gamma}_r \frac{f}{50}$$

où f représente la fréquence réelle.

La viscosité dynamique η a été calculée par rapport à la tension de cisaillement τ_r et le gradient $\dot{\gamma}_c$ en employant la relation:

$$\eta = \frac{\tau_r}{\dot{\gamma}_r} 100$$

où η représente la viscosité dynamique en cP.

Pendant les recherches on a poursuivi la variation de la viscosité de l'apprêt par rapport à la vitesse de cisaillement pour son augmentation et aussi pour sa diminution. On a recherché des apprêts pour l'encollage en amidon préparés à l'aide de deux technologies: l'ébullition sous pression et cavitation hydroacoustique. La tehnologie du scindement de l'amidon par cavitation hydroacoustique engendre les chaudières pour la préparation et les gardes habituelles parmi lesquels on monte une installation speciale de cavitation qui assure le circuit fermé de l'apprêt à l'aide d'une pompe. On a utilisé deux variantes technologiques:

a) La scission par cavitation simultanément à la dilatation thermique des grains d'amidon.

b) La scission par cavitation à la suite du processus de dilatation thermique des grains.

On a expérimenté des apprêts avec deux concentrations différentes en amidon (11% et 7%) en obtenant plusieurs variantes d'expérimentation à la suite de la combination avec les deux variantes technologiques ci-dessus.

Avec les résultats obtenus des expériments on a construit les graphiques (voir Figs.2,...,7) à partir de desquels on peut tirer plusieurs conclusions.

Ainsi, aux concentrations plus élevées en amidon (11%) la préparation de l'apprêt avec scission par cavitation hydroacoustique peut être faite seulement par le déployement concomitant de la cavitation et de la dilatation thermique des grains.

Pendant l'étape d'augmentation de la température d'apprêt jusqu'à 70-75°C a lieu une remarquable augmentation de la viscosité (3 333,333 cP a une valeur $\dot{\gamma}$=16,2 s^{-1}) bien (encore) que le processus de cavitation a (ait) lieu en même temps. À ces concentrations plus élevées l'effet de la dilatation thermique est plus puissant que l'effet de la scission par cavitation hydroacoustique. Même après 15 minutes de cavitation hydroacoustique l'apprêt a un puissant caractère thixotrope avec une structure interne encore nonhomogène et avec puissantes variations en temps (Fig.2). Par example, au même gradient de la vitesse de cisaillement ($\dot{\gamma}$=16,25 s^{-1}) la variation de la viscosité entre les deux courbes de thixotropie est 44%. L'obtention d'une courbe hystéresis ouverte fait preuve d'un apprêt avec une structure nonhomogène avec un degré de scindement insuffisant de l'amidon. Le prolongement du temps de

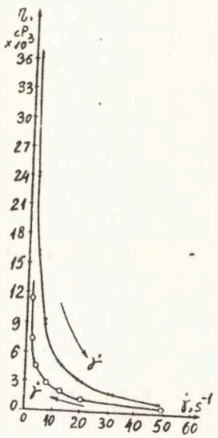

Fig. 2

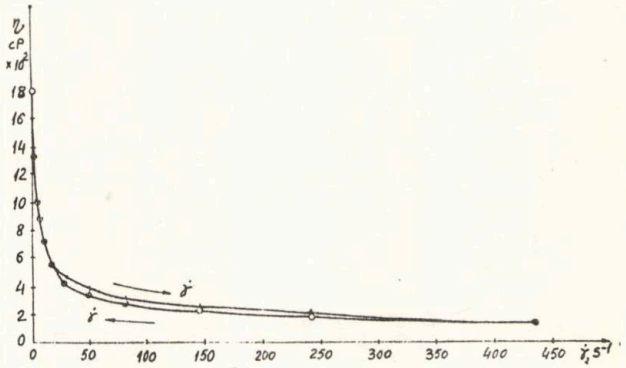

Fig. 3

la scission par cavitation jusqu'à 30 min. à une temperature de 75-80°C, mène vers la réduction de la caractéristique thixotrope de l'apprêt (Fig.3).

On obtient ainsi un apprêt plus homogène et avec un accentué degré de scindement même sans l'ébullittion ou l'utilisation des auxiliaires chimiques.

La caractéristique de thixotropie a été beaucoup réduite en avançant vers les comportaments pseudoplastiques.

La viscosité a six fois baissés et la thixotropie avec plus de 40% (correspondant à une valeur $\dot{\gamma}$=16,25 s^{-1}).

La préparation des apprêts pour l'encollage avec des concentrations plus petites (7% amidon) l'augmentation de la viscosité dans l'étape de la dilatation thermique des grains (50-80°C) est faite à des valeurs plus baissées de celle-ci (Fig.4).

Dans cet intervalle des tempèratures (40-80°C) le processus de la dilatation thermique des grains et de l'augmentation de la viscosité a aussi un effet plus important

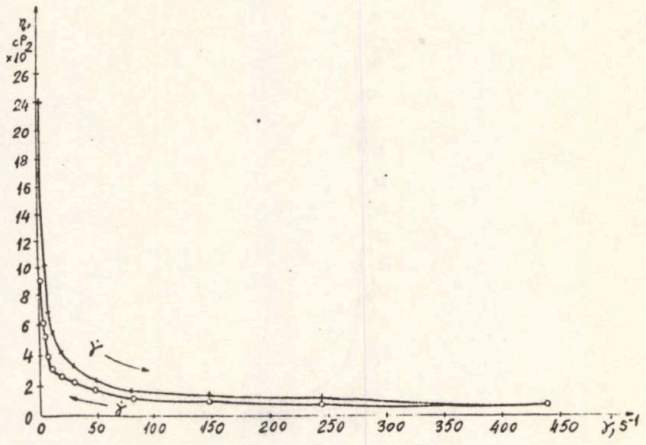

Fig. 4

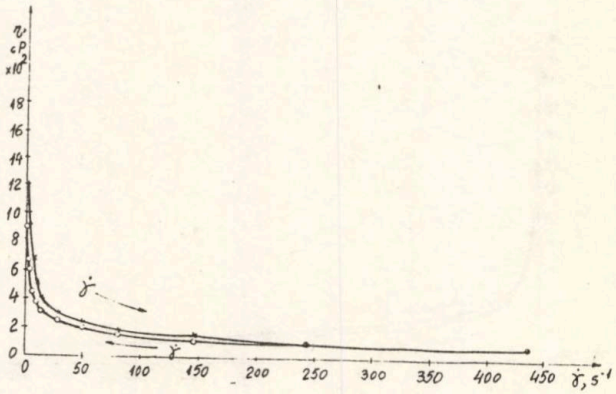

Fig. 5

que le processus de la diminution de la viscosité par cavitation hydroacoustique.

Parmi ces deux processus aux effets contraires à des concentrations plus petites en amidon la diminution de la viscosité a moins d'importance. Voilà pourquoi le déployement du processus de cavitation en même temps avec celui de dilatation thermique n'est pas forcément necessaire.

L'efficacité du scindement par cavitation matérialisé par la diminution de la viscosité est moins évidente (Figs.4, 5). L'efficacité du processus de scindement par cavitation commence à augmenter visiblement dans l'intervale de température 75-85°C.

Le déployement du processus de cavitation pendant 7-8 minutes à cette température a un effet foudroyant de réduction de la viscosité jusqu'aux valeurs desirées.

Le scindement par cavitation contribue dans la plupart à la diminution de la

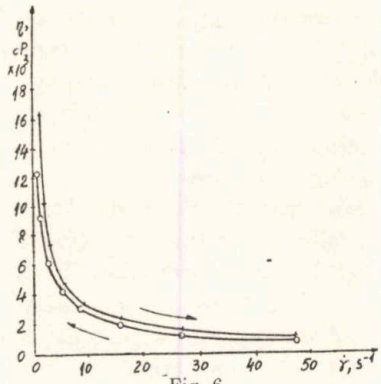

Fig. 6

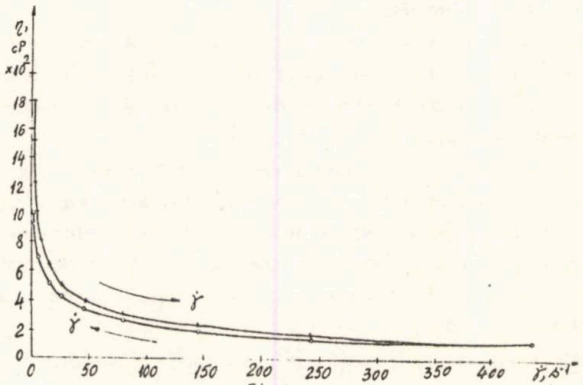

Fig. 7

caractéristique de thixotropie de l'apprêt.

L'efficience de la cavitation vers la diminution de thixotropie est aussi évidente dans l'intervalle des temperatures: 70-85°C. On peut constater des diminutions de thixotropie avec 7-22,5% correspondant aux differentes valeurs de la vitesse de cisaillement, entre 16,2 s^{-1} et 1 s^{-1}.

À partir de ces conclusions on a expérimenté la technologie de préparation de l'apprêt dont le scindement par cavitation de l'amidin commence après sa dilatation, thermique granulaire. Une telle technologie de préparation avec cavitation pour le scindement succesif à la dilatation thermique est plus convenable du point de vue de la consommation de l'énergie et permet un contrôle plus facile du processus de scindement et de la qualité de l'apprêt.

À base des recherches faites sur la viscosité et la thixothropie d'apprêt obtenu par cette variante technologique de preparation reflétée dans les représentations graphiques 6 et 7 on peut tirer quelques conclusions pratiques. Ainsi, la même concentration en amidon (7%), l'échauffement d'apprêt jusqu'à 75-80°C sans cav-

itation de scindement (Fig.4) mène au toucher des viscosités maxima six fois plus élevées en comparaison avec le variante technologique avec déployement concomitant de ces deux processus (Fig.5). C'est pourquoi la technologie avec deployement successif des processus d'échauffement et de cavitation hidroacoustique peut être utilisée seulement aux apprêts avec des concentrations plus ou moins réduites (8%).

Le commencement de la scission par cavitation à 80°C après la dilatation thermique des grains a les conséquences suivantes:

– la diminution de la caractéristique thixotrope de l'apprêt à partir d'une différence de 20-4000 cP à une difference de 200-1800 cP après dix minutes de cavitation à une difference de 100-240 cP seulement apres 15 minutes de cavitation;

– le toucher des caractéristiques de viscosité et de thixotropie de l'apprêt préparé par cavitation similaire à celui de l'apprêt préparé par ébullition sous pression s'obtient après maximum 10 minutes de cavitation;

– la diminution de la viscosité de l'apprêt environ 3,4-2,4 fois après seulement 10 minutes de cavitation hydroacoustique et de 9-4 fois après 15 minutes de cavitation (Figs.6 et 7 en comparaison avec 4);

– la diminution continue de la viscosité de l'apprêt apres l'accouplement de l'installation de cavitation permet un contrôle plus facile du scindement par l'opérateur en donnant la possibilité d'arrêt du processus de cavitation au toucher de la viscosité nécessaire à l'encollage (10-15 minutes).

2. Conclusions. a) La nouvelle technologie de préparation de l'apprêt d'encollage peut avoir lieu en deux variantes. Le scindement par cavitation en même temps avec la dilatation thermique des grains d'amidon aux concentrations plus élevées et scindement par cavitation succesive à la dilatation thermique des grains aux apprêts aux concentrations plus petites. Plus avantageuse est la deuxième variante technologique du point de vue economique et technique.

b) Les études effectuées sur la thixotropie des apprêts d'amidon obtenues par la nouvelle variante technologique de scindement de l'amidon ont montré une diminution importante de cette caractéristique même aprés 15 minutes seulement de cavitation hydroacoustique.

c) Les apprêts obtenus par cavitation hydroacoustique présentent un degré plus élevée d'homogénéité pour le processus de scindement. Ces caractéristiques ameliorées vont permettre un encollage plus uniforme des fils et des indices techniques et économiques superieurs dans le tissage.

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CONTRIBUŢII LA CERCETAREA VISCOZITĂŢII APRETULUI DE ÎNCLEIERE PE BAZĂ DE AMIDON CU SCINDARE PRIN CAVITAŢIE HIDROACUSTICĂ

(Rezumat)

Sunt prezentate rezultatele cercetărilor efectuate asupra tixotropiei apreturilor de încleiere preparate prin două variante tehnologice de scindare a amidonului. Apreturile preparate prin cavitaţie hidroacustică concomitentă sau succesivă dilatării termice a granulelor se caracterizează printr-un înalt grad de omogenizare a structurii interne şi diminuare a caracteristicilor tixotrope ale apretului.

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Secţia VIII
TEXTILE. PIELĂRIE

ALGORITHM FOR THE CALCULATION OF THE COMPACTNESS DEGREE OF DOUBLE WOVENS
IV. THE COMPACTNESS DEGREE OF DOUBLE WOVENS WITH STITCHING WARP

BY
DANIEL CHINCIU, IRINA CRISTIAN and GABRIEL CHINCIU

It is presented an algorithm for CAD for the calculus of the compactness degree of the double wovens with stitching warp with an alternance of 1 US : 1 UIs : 1 UI for the warp systems and 1 BS : 1 BI for the weft systems.
The algorithm is IBM compatible.

1. Introduction. Stitching with special yarns of compound wovens complicates the fabrication technology, yet without inducing significantly different tresses between the yarn systems forming the two wovens. This later aspect is less obvious when applying stitching with warp system beeig nevertheless more pregnant for stitching with weft system, a case in which – for some unsuitably selected links of the woven's upper side – negative influences may be manifested on its surface aspect.

The compactness degree for double wovens, involving stitching with special warp or weft yarns, may be calculated for each system of yarns in the wovens with the following relations:

$$Ku_x = \frac{Pu_x \cdot L_{Ru_x}}{Ru_x}, \tag{1}$$

$$Kb_y = \frac{Pb_y \cdot L_{Rb_y}}{Rb_y}, \tag{2}$$

where x and y represent the warp and, respectively weft fibers of the double woven.

The compactness degree of the double woven may be calculated by summing up the compactness degree on the yarn systems with relation:

$$Kt = \frac{\sum_{x=1}^{m} Ku_x + \sum_{y=1}^{n} Kb_y}{m+n}, \tag{3}$$

where: m – number of warp systems in the double woven's structure, n – number of weft systems in the same woven.

2. Calculation of the Compactness Degree for Double Wovens with Stitching Warp for an Alternance Ratio 1:1 (LD – UI). The block diagram, the

partial and general drawings of a double link with stitching warp are presented in Figs.1 and 2.

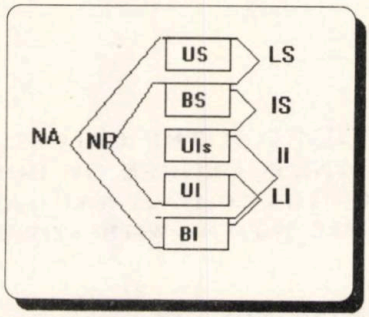

Fig. 1.– Block diagram of a double link with stitching warp.

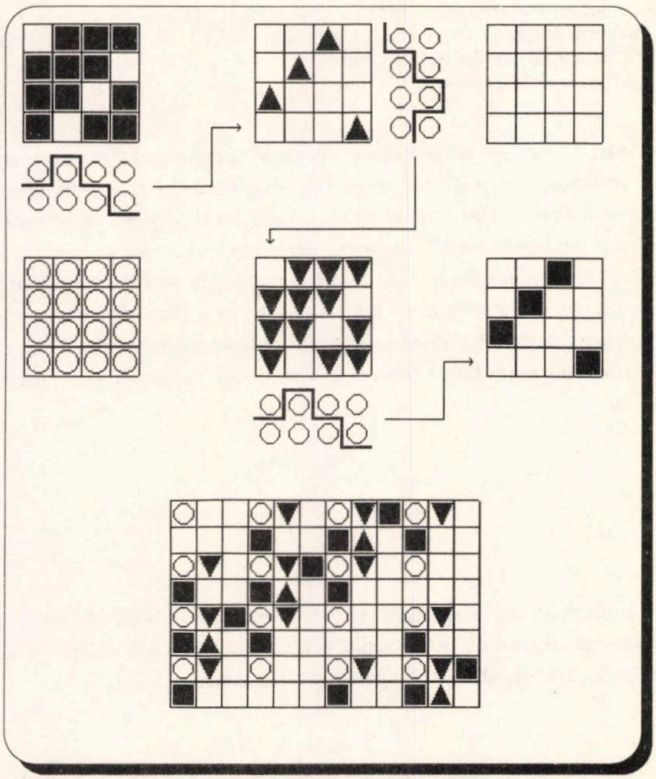

Fig. 2.– Double woven with stitching warp.
Partial drawings. General drawing of the link.

3. Calculation of the Compactness Degree of the Warp Systems. Length of the warp ratio for the three warp yarn systems, at maximum technological thickness,

may be calculated – as based on Fig.3 – with relations:

$$L_{Ru_s} = Ru_s \cdot d_{u_s} + (D_s \cos\beta_s - d_{u_s}) \cdot t_{b_s}, \tag{4}$$

$$L_{Ru_{In}} = Ru_{In} \cdot d_{u_{In}} + x_{b_{In_s}} t_{b_{In_s}} + x_{b_{In_i}} t_{b_{In_i}}, \tag{5}$$

$$L_{Ru_i} = Ru_i \cdot d_{u_i} + (D_i \cos\beta_i - d_{u_i}) \cdot t_{b_i}, \tag{6}$$

where:

$$x_{b_{In_s}} = Lu_{In_s} - d_{u_{In}}, \tag{7}$$

$$x_{b_{In_i}} = Lu_{In_i} - d_{u_{In}}, \tag{8}$$

$$Lu_{In_s} = (d_{u_{In}} + d_{b_s}) \cos\beta_{In_s} = D_{In_s} \cos\beta_{In_s}, \tag{9}$$

$$Lu_{In_i} = (d_{u_{In}} + d_{b_i}) \cos\beta_{In_i} = D_{In_i} \cos\beta_{In_i}, \tag{10}$$

where from there results:

$$L_{Ru_{In}} = Ru_{In} \cdot d_{u_{In}} + (D_{In_s} \cos\beta_{In_s} - d_{u_{In}}) \cdot t_{b_{In_s}} + (D_{In_i} \cos\beta_{In_i} - d_{u_{In}}) \cdot t_{b_{In_i}}. \tag{11}$$

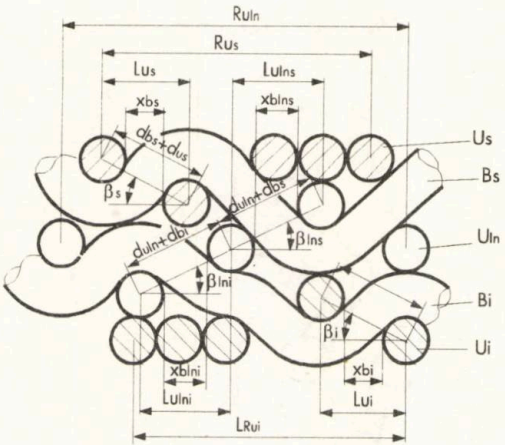

Fig. 3.– Double woven with stitching warp. Cross section. Minimum geometrical thickness.

By successively replacing (9), (10) and (11) in relation (1), the calculation relations for the compactness degree of the warp systems may be obtained:

$$Ku_s = \frac{Pu_s[Ru_s \cdot d_{u_s} + (Ds \cos\beta_s - d_{u_s}) \cdot t_{b_s}]}{Ru_s}, \tag{12}$$

$$Ku_{In} = \frac{Pu_{In}[Ru_{In} d_{u_{In}} + (D_{In_s} \cos\beta_{In_s} - d_{u_{In}}) \cdot t_{b_{In_s}} + (D_{In_i} \cos\beta_{In_i} - d_{u_{In}}) \cdot t_{b_{In_i}}]}{Ru_{In_s}}, \tag{13}$$

$$Ku_i = \frac{Pu_i[Ru_i \cdot d_{u_i} + (Di \cos\beta_i - d_{u_i}) \cdot t_{b_i}]}{Ru_i}. \tag{14}$$

The observation was made that the stitching warp links both the upper and the lower weft, which is also reflected in the calculation of the compactness degree for

stitching warp, where: Ku_{In} – the compactness degree for stitching warp; Pu_{In} – geometrical thickness of the stitching warp; Ru_{In} – warp ratio of the stitching warp; $d_{u_{In}}$ – diameter of the stitching warp; D_{In_s}, D_{In_i} – sum of the diameters of the superior stitching warp and weft fibres, respectively sum of the diameters of the inferior warp and weft stitching fibres; β_{In_s} – waving angle of the stitching warp caused by linking with the superior weft; β_{In_i} – waving angle of the stitching warp caused by linking with the inferior weft; $t_{b_{In_s}}$ – number of the upper weft shiftings between the fibers of the stitching warp within a ratio; $t_{b_{In_i}}$ – number of the lower weft shiftings between the fibers of the stitching warp within a ratio.

4. Calculation of the Compactness Degree in Weft. Length of the weft ratio for the two weft yarn systems, at maximum technological thickness, may be calculated – from Fig.4 – with the following relations:

$$L_{Rb_s} = Rb_s d_{b_s} + x_{u_s} t_{u_s} + x_{u_{In_s}} t_{u_{In_s}}, \tag{15}$$

$$L_{Rb_i} = Rb_i d_{b_i} + x_{u_i} t_{u_i} + x_{u_{In_i}} t_{u_{In_i}}, \tag{16}$$

where:

$$x_{u_s} = Lb_s - d_{b_s} = (D_s \cos \alpha_s - d_{b_s}), \tag{17}$$

$$x_{u_{In_s}} = Lb_{In_s} - d_{b_s}, \tag{18}$$

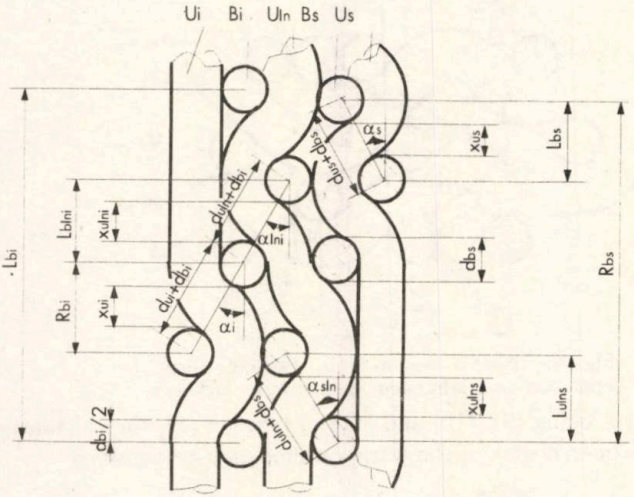

Fig. 4.– Double woven with stitching warp. Longitudinal section. Minimum geometrical thickness.

$$Lb_{In_s} = (d_{u_{In}} + d_{b_s}) \cos \alpha_{In_s} = D_{In_s} \cos \alpha_{In_s}, \tag{19}$$

$$x_{u_i} = Lb_i - d_{b_i} = (D_i \cos \alpha_i - d_{b_i}), \tag{20}$$

$$x_{u_{In_i}} = Lb_{In_i} - d_{b_i}, \tag{21}$$

$$Lb_{In_i} = (d_{u_{In}} + d_{b_i}) \cos \alpha_{In_i} = D_{In_i} \cos \alpha_{In_i}. \tag{22}$$

From these relations there results:

$$L_{Rb_s} = Rb_s d_{b_s} + (D_s \cos\alpha_s - d_{b_s}) t_{u_s} + (D_{In_s} \cos\alpha_{In_s} - d_{b_s}) t_{u_{In_s}}, \quad (23)$$

$$L_{Rb_i} = Rb_i d_{b_i} + (D_i \cos\alpha_i - d_{b_i}) t_{u_i} + (D_{In_i} \cos\alpha_{In_i} - d_{b_i}) t_{u_{In_i}}. \quad (24)$$

By successively substituting (23) and (24) in relation (2), the relations for the calculation of the weft's compactness degree may be obtained:

$$K'b_s = \frac{Pb_s[Rb_s d_{b_s} + (D_s \cos\alpha_s - d_{b_s}) t_{u_s} + (D_{In_s} \cos\alpha_{In_s} - d_{b_s}) t_{u_{In_s}}]}{Rb_s}, \quad (25)$$

$$K'b_i = \frac{Pb_i[Rb_i d_{b_i} + (D_i \cos\alpha_i - d_{b_i}) t_{u_i} + (D_{In_i} \cos\alpha_{In_i} - d_{b_i}) t_{u_{In_i}}]}{Rb_i}, \quad (26)$$

where: α_{In_s} – the waving angle of the superior weft due to the link with the stitching warp; α_{In_i} – the waving angle of the inferior weft due to the link with the stitching warp; $t_{u_{In_s}}$ – number of the shiftings of the stitching warp between the fibers of the superior weft within a ratio; $t_{u_{In_i}}$ – number of the shiftings of the stitching warp between the fibers of the inferior weft within a ratio.

5. Conclusions. The calculation algorithm of the compactness degree discussed in the present study permits the establishment of some methods of designing double wovens with stitching warp, as a function of the degree of compactness required, as a parameter defining a woven material in the most complet mode.

The value of compactness degree depends both on the thickness and fineness (expressed throught the diameter) of the yarn systems, as well as by the linking applied.

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ALGORITM DE CALCUL AL GRADULUI DE COMPACTITATE PENTRU ŢESĂTURI DUBLE

IV. Gradul de compactitate pentru ţesături duble cu urzeală de însăilare

(Rezumat)

Algoritmul prezentat pentru calculul gradului de compactitate este conceput pentru proiectarea asistată de calculator a ţesăturilor duble cu urzeală de însăilare la care raportul de alternanţă al firelor de urzeală şi bătătură este 1US:1UIs:1UI şi respectiv 1BS:1BI. Algoritmul corespunde condiţiilor de portabilitate pe calculatoarele compatibile IBM PC, în orice limbaj de programare.

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TEXTILE. PIELĂRIE

PRESSING TECHNOLOGICAL PROCESS DESIGN USING VALUE ENGINEERING

BY

PULFERIA NICOLAIOV, COSTACHE RUSU and IRINA IONESCU

The aim of the paper is the elaboration of the practical methodology for the Value Engineering application in pressing processes designing. The concrete possibilities for taking over the necessary information were considered, as well as the cost elements recorded in the apparel plants

1. The Objective and Opportunity of the Research. The aim of the pressing functional design using value engineering is the very best planed level for garment's functions materialized in conditions of economical efficiency.

The motivation of the research is argumented by the complexity of the pressing technology and by the great importance in the garment's quality assurance.

German Standard DIN 8580 defines pressing process as a process of fabric modification and stabilisation due to fabric's maleability and plasticity. A percentage of 60% of garments quality requires refers to the shape, dimension and stability of garment's lines and surfaces.

The paper's aim is to elaborate a practical methodology of value engineering application in pressing process design.

2. Method of the Value Analysis at the Pressing Process Level. The essential principle for the elaboration of the functional design model of pressing process represents the extension of the general algorithm used by the value analysis at garment level [1].

The design method proposed in this paper is given into account the effective possibilities for taking over the necessary information and the evidence modalities of cost elements in apparel plants.

2.1. The List of the Pressing Process Functions Elaboration. The pressing technological process can be descomposed in primary events, similar to elementary using values at garment level and technological blocks able to ensure their objectives materialisation at a garment style level.

The primary events reflect the content of the physique-mechanical actions upon the semimanufactured goods; these are typical for the pressing technological objectives that provides the structure and dimension of the technological programme at every phase of the pressing process level.

The general technological objectives of the pressing process are constituted in processes' functions F_i (Table 1).

Table 1

Function	Function's Name	Technical Dimensions (dt_i)	Useful Domain (dt_M-dt_m)
F_1	Surfaces Levelling	Rumpling Indicator, π	0 – for main fabric 0.28-0.5 for linings
F_2	Forming	$\alpha=aP^n$ (degrees) variation of the angle between the warp and filling yarns H, l, s (mm) – dimensional paramethers for the formed area	10-15 degrees
F_3	Seam Allowances Ironing on One Side	α (degrees) flatten angle of the seam allowances	23-25 degrees
F_4	Seam Allowances Ironing on Oposite Sides	"	"
F_5	Pleating	α,degrees, opening angle	15-23 degrees
F_6	Creasing (edge folder)	"	"
F_7	Edge Pressing	δ (%), the depth loss degree	17-37%
F_8	Steaming	Changing of the shining degree (%)	<20%
F_9	Goffering	y (mm) the deformation depth	80% of the template penetration depth
F_{10}	Heat-setting and Hygro-chemio-heat setting	λ (%) decreasing changing of the shining degree	<20%

The essential technological effects of pressing, measured on garment, represent the technical dimensions (dt) of F_i functions and they have direct implications on the function dimensions of the garment and on its using value (Table 2).

At planed level the technic dimensions of the F_i functions are materialised in sets of pressing and final finishing operations structurated in main blocks (B_i) and subordinated blocks b_{ij}.

Technological blocks b_{ij} are adapted as block functions of the pressing process design [2], [3].

The structure of the function list b_{ij} is dimensioned in relation with the essential features of pressing for each of the garment's type and style.

The identity of the block functions b_{ij} is establised for every garment style for the elementary pressing areas. For each elementary area there is a block functions b_{ij} which technological objective is correlated with its paramethers (dimensions, structure, the necessary content of the pressing process).

The block functions b_{ij} have not their own technical dimensions measured by physique values. The importance level (the percentage in garment's using and appearence value) can be expressed by atributes, evaluated by examination method [4] so that the functions can be hierarchied.

2.2. The Economic Dimension of F_i&b_{ij} Functions. The economic dimensioning of the b_{ij} functions is directly made regarding labor costs for pressing operations and overhead costs.

Table 2

Interferences between the Garment Functions and Primary Functions F_i (men jacket)

Garment Functions	Process Functions F_i						
	F_1	F_2	F_3	F_4	F_6	F_7	F_8
Garment Appearance	*	*	*	*	*	*	*
Technological Processing Style Effect	*	*	*	*	*	*	*
Dimensional Correspondence Body-Garment		*					*
Psyhosenzorial Confort	*		*	*			*
Size and Shape Stability	*	*		*	*	*	*
Easy Maintenance		*			*	*	*

Table 3

A Part of the b_{ij} Functions List for Men Jacket

$B_i; b_{ij}$	$B_i \& b_{ij}$ Identity
B_1	Front
b_{11}	Forming and Levelling the Bust Area
b_{12}	Forming and Pressing the Handkerchief Pocket
b_{13}	Forming and Pressing the Side Pocket
b_{14}	Edges Forming and Pressing
b_{15}	Lapel Forming and Pressing
b_{16}	Folding and Creasing Bottom Hem
B_2	Back ($b_{21}...b_{24}$)
B_3	Sleeve ($b_{31}...b_{33}$)
B_4	Essential Seams ($b_{41}...b_{43}$)
B_5	Lining (b_{51})

The economic dimensioning of the F_i functions can be indirectly made by identifing the interferences between $F_i \& b_{ij}$ at a garment level (Table 4). The cost distribution on F_i functions can be made using an importance level matrix. These can be worked out by logical engineering judgements.

Table 4

Labor Costs Distribution for $F_i \& b_{ij}$ (part of the table for men jacket)

$B_i; b_{ij}$	The name of the operation	Operation cost (lei)	Functions F_i						
			F_1	F_2	F_3	F_4	F_6	F_7	F_8
B_1									
b_{11}	ironing side seam	110			*				*
	front forming on the bust area	110	*	*					*
	final pressing of the upper front area	200	*	*					*
	Total	420							
b_{12}									
b_{13}									
...									
b_{51}									
	Total cost F_i (lei)		(lei)	(lei)	(lei)	(lei)	(lei)	(lei)	(lei)

2.3. The Model of the Functional Designing of the Pressing Process. Now, the general draft for the model of the functional designing of the pressing process can be

formulated.

The designing and improving of the technological pressing process by using value engineering provide the outlining and quantifications of the interferences between these and garment quality (Fig.1).

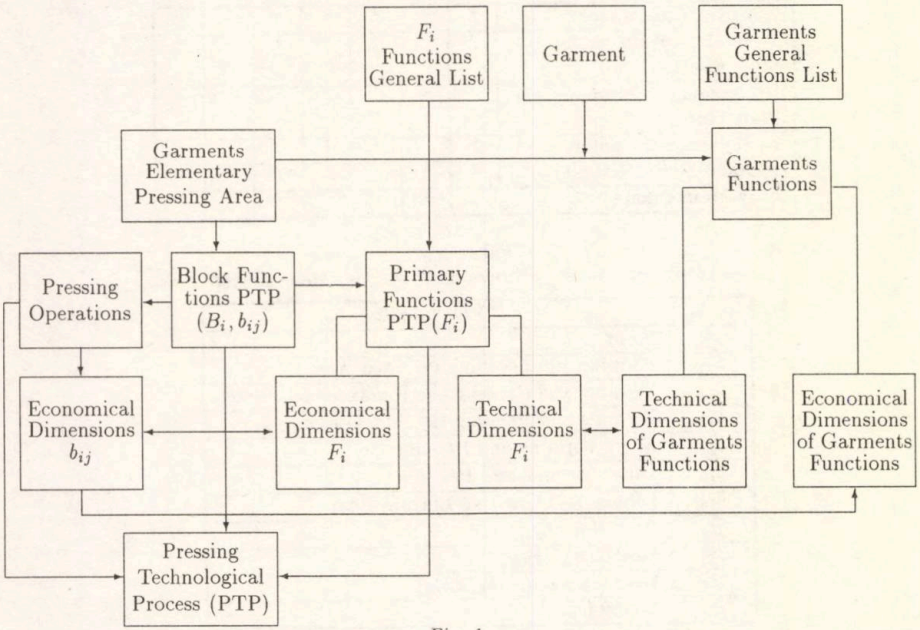

Fig. 1

In the mean time effective ways of action can be established in processes quality management for improving the garments quality performances.

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PROIECTAREA PROCESELOR TEHNOLOGICE UMIDOTERMICE FOLOSIND INGINERIA VALORII

(Rezumat)

Lucrarea îşi propune elaborarea metodologiei practice de aplicare a ingineriei valorii în proiectarea şi optimizarea proceselor de tratare umidotermică, având în vedere şi posibilităţile concrete de preluare a informaţiilor necesare şi modalităţile de evidenţă a elementelor de cost în cadrul întreprinderilor de confecţii.

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Secţia VIII
TEXTILE. PIELĂRIE

LA GRADUATION DES REPÈRES IRRÉGULIERS

BY

GABRIELA MĂLUREANU, MARIANA COCEA et CODRINA RĂDĂVOI

Dans ce travail on a étudié la graduation des repères des produits des chaussures, une étape de très grande importance dans la préparation de la fabrication et on a présenté un programme implémanteé sur un ordinateur IBM-PC qui donne la possibilité d'obtenir une série de pointure d'un repère.

1. Introduction. La projection constructive d'un nouveau modèle destiné à la fabrication industrielle est réalisée courramment pour la pointure moyenne de la série particulière, pur laquelle on recommande le modèle.

On obtient les repères composant toute la série des pointures par l'opération de multiplication partant dans ce sens des patrons correspondants à la pointure moyenne et utilisant les lois de variation des dimensions des patrons dans le système particulier de graduation.

Dans la préparation de la fabrication, la graduation des repères en série de pointure constitue une étape de très grande importance, aux implications directes sur l'assurance de la qualité des usinages technologiques ultérieurs (l'assemblage des repères, la formation spatiale du demiproduit, l'execution correcte de certains S.D.V.) et finalement sur la qualité des produits.

Le manque de respect des lois de variation dimensionnelle des patrons à la graduation peut constituer une source d'erreurs dimensionnelles ayant des influences sur la concordance dimensionnelle entre les lignes commes de contour des repères à l'assemblage et aussi la concordance dimensionnelle entre le demiproduit et l'embauchoir dans le processus de la formation spatiale.

Par conséquant, la connaissance et la soumission aux principes généraux de variation dimensionnelle des patrons en série de pointure est un élément de très grande importance dans la réalisation correcte de la graduation des patrons dans la fabrication en série.

2. Les lois de variation dimensionnelle à la graduation dans le système arithmétique. Ayant en vue la nécessité du moulage très fidèle du demiproduit sur l'embauchoir dans le processus de la formation spatiale, de la concordance dimensionnelle entre les repères rigides et la superficie de la plante de l'embauchoir, la réalisation correcte de l'opération de graduation des patrons devra être réalisée dans les conditions de la connaissance et de la soumission aux lois de variation des dimensions des embauchoirs en série de pointure, embauchoirs sur lesquels on forme,

on assemble et on fait le finissage des produits [1], [2].

2.1. La variation des dimensions de base des embauchoirs en série de pointure. Les études antropométriques effectuées dans la plupart des pays à une industrie de chaussure dévelopée ont permis d'établir certains lois de variation des paramètres antropométriques du pied pendant une sélection représentative de consommateurs.

Étudiant ces informations biométriques on est arrivée à définir les lois de variation de la dimension du pied d'une pointure à l'autre et à partir d'effes on a établi les lois de transformation des caractéristiques dimensionnelles des embauchoirs en série de pointure et largeur.

On a élaboré ainsi, dans la plupart des pays, des tableaux concernant les dimensions de base des embauchoir à l'intérieur des séries de pointure et de largeur pour un certain groupe de consommateurs [3], [4].

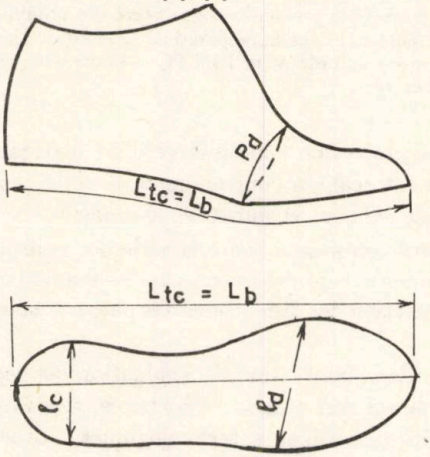

Fig. 1

La dimension longitudinal de base de l'embauchoir $L_{tc} = L_b$ (la longueur de la plante de l'embauchoir est idéntique à la longueur de la semelle principale), Fig.1, varie à l'intérieur de la série de pointure, par le passage d'une pointure à une autre, avec une dimension constante, selon une relation telle que:

$$Y_{Nn+1} = Y_{Nn} + \Delta Y_N,$$

où: Y_{Nn} est la dimension $L_{tc} = L_b l_0$ à l'embauchoir correspondant au numéro de dimension N_n de la série; Y_{Nn+1} – la dimension $L_{tc} = L_b l_0$ à l'embauchoir de dimension N_{n+1}; ΔY_N – l'augmentation L_{tc} par le passage d'une pointure à une autre dans la même série.

L'augmentation ΔY_N est dépendante au point de vue de la valeur du système de numérotage des embauchoirs tel que:

Table 1

ΔY_N	Le système de numérotage		
	métrique	français	anglais
$L_{tc} = L_b$	5 mm	1 stich=1 p.c.=6,6 mm	1/6 inch=4,23 mm

Pour les dimensions transversales de base de l'ambauchoir (P_d; P_r; l_d; l_c), on peut aussi écrire des relations similaires, à l'intérieur de la série de pointure, respectivement largeurs, comme par exemple:

$$X_{Nn+1,G} = X_{Nn,G} + \Delta X_N,$$

c'est-à-dire les dimensions transversales de base varient par le pasage d'une pointure à une autre ($N_n \rightarrow N_{n+1}$) à l'intérieur d'une série ayant une constante ΔX_N, dépendante du point de vue de la valeur du système de numérotage et du paramètre particulier mis en discussion et respectivement:

$$X_{N,G+1} = X_{N,G} + \Delta X_G,$$

c'est-à-dire les dimensions transversales de base de l'embauchoir pointure N varient par le pasage d'une largeur à une autre ($G \rightarrow G + 1$) à l'intérieur d'une série à une dimension constante ΔX_G, dépendante valoriquement du système du numérotage, de la destination et du paramètre particulier mis en discussion (périmètre ou largeur numérotés).

À l'intérieur du système métrique, système utilisé chez nous aussi, conformément STAS 29122/1986, ces augmentations sont, par exemple, pour le périmètre aux doits (P_d) et la largeur aux doits (l_d):

Table 2

Destination	$\Delta P_d/N_m$	$\Delta P_d/G$	$\Delta l_d/N_m$	$\Delta l_d/G$
enfants, filles, garçons adolescents, adolescentes	3,5	5	1,3	1,9
femmes	3	6	1,1	2,2
hommes	3	7	1,1	2,6

Conformément aux informations de la littérature, dans le système français de numérotage des embauchoirs l'augmentation du périmètre aux doits (ΔP_d) est de 4 mm au passage d'une pointure à une autre de la série (par exemple, $36 \rightarrow 37 \rightarrow 38...$), et d'une largeur à une autre l'augmentation ΔP_d est de 5 mm.

Dans le système anglais de numérotage, l'augmentation du périmèter aux doits de l'ambauchoir (ΔP_d), par le passage d'une pointure à une autre de la série, est de 2,5 mm (par exemple, $4 \rightarrow 4,5 \rightarrow 5$) et de 5 mm par le passage d'une largeur à une autre.

Il est possible que, fonction de particularités dimensionnelles des pieds des consommateurs d'un certain pays, les augmentations ΔL_{tc} et ΔP_d soient adaptées aux autres valeurs que celles déjà mentionnées; c'est pourqois lorsqu'on travaille pour des patenairs étrangers, on les déterminera, par le mesurage, directement sur le série d'embauchoir..

2.2. La variation des dimensions de base des patrons en série de pointures. La multiplication des repères en série devra être réalisée sur les mêmes principes arithmétiques de variation dimensionnelle qui constituent les lois de variation dimensionnelle du pied et qui sont à la base des lois de variation des dimensions lesquels on forme, on assemble et on fait le finissage du produit.

Ce principe général arithmétique a à la base la relation:

$$N_{\pm n} = N_0 \pm n\Delta N,$$

où $N_{\pm n}$ est la pointure; N_0 – la pointure de base de la série; ΔN – l'augmentation absolue d'une pointure à une autre, dépendante directement du système de numérotage employé; n – échelon d'augmentation ou de diminution égal à la différence entre le numéro de base N_0 et le numéro $N_{\pm n}$ qui va être obtenu, exprimé en pointures.

Tenant compte de l'existence des certains augmentations dimensionnelles différenciées au sens longitudinal et transversal tant au pied que l'embauchoir, la multiplication des repères sera faite avec les distinctions de valeurs numériques sur les deux directions principales: longitudinale et transversale, conformément aux relations similaires (Fig.2):

$$L_{\pm n} = L_0 \pm n\Delta L, \qquad l_{\pm n} = l_0 \pm n\Delta l,$$

où: L_0, l_0 sont la longueur, respectivement la largeur du patron correspondant à la pointure de base; ΔN – l'augmentation absolue du patron au sens longitudinal, par le passage d'une pointure à une autre de la série; Δl – l'augmentation absolue du patron au sens transversal, par le passage d'une pointure à une autre de la série.

Les relations peuvent être transcrites sous la forme suivante:

$$L_{\pm n} = L_0\left(1 \pm n\frac{\Delta L}{L_0}\right) = L_0(1 \pm n\alpha), \quad l_{pmn} = l_0\left(1 \pm n\frac{\Delta l}{l_0}\right) = l_0(1 + n\beta),$$

où $\Delta L/L_0$ et $\Delta l/l_0$ représentent l'augmentations relatives dans les deux directions du patron, c'est-à-dire sur la direction longitudinale et transversale [1].

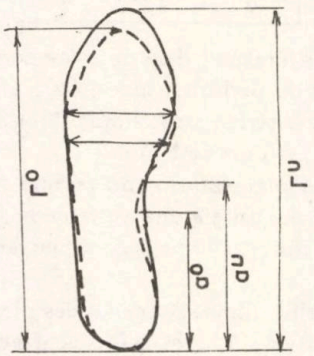

Fig. 2

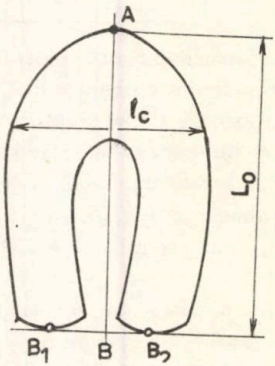

Fig. 3

La longueur particulière de $a_0 \neq L_0$ apartenant au patron N_0 va se modifier selon une relation similaire par le passage à une numéro N_n par la graduation:

$$a_n = a_0(1 \pm n\alpha).$$

L'application des relations de multiplication qui contient les augmentations relatives est nécessaire parce qu'on ne multiple pas toujours l'ensemble tout entier.

La largeur particulière b_0 se modifiera par le pasage d'une pointure à une autre à l'intérieur de la série selon la relation:

$$b_n = b_0(1 \pm n\beta).$$

Les augmentations absolues ΔL et Δl dépendent directement du système de numérotage de l'embauchoir (métrique, français, anglais) et il faut aussi être particularisée pour les deux ensembles du produit: supérieur, respectivement inférieur.

3. Le calcul des augmentations relatives à la graduation de l'ensemble supérieur. Pour la détermination des augmentations relatives utilisées à la graduation des repères de l'ensemble supérieur de la chaussure on considère le dessin de base des faces (Fig.3), qui correspon à la pointure N_0, sur lequel on peut déterminer les deux dimensions de base, la longueur L_0 et la largeur l_0.

La longueur totale (L_0) du dessin de base est mesurée le long de la médiane entre le point extrême antérieur A et le point B, obtenu par le tracement d'une perpendiculaire sur l'axe longitudinale du dessin la tangente aux points extrêmes B_1 et B_2.

La largeur totale du dessin de base (l_0) est mesurée dans la région des doits (1/3 de la longueur du dessin) sur une direction perpendiculaire à l'axe longitudinale du dessin, dans la zone de maxime largeur.

L'augmentation absolue (ΔL) du dessin de base des faces représentant l'augmentation de la longueur totale (L_0) du dessin de base par le passage d'une pointure à une autre à l'intérieur de la série de pointure s'adopte égale en dimension à l'augmentation de la longueur de la plante de l'embauchoir d'une pointure à une autre en série et donc, elle sera différenciée par rapport au système de numérotage:

ΔL=5 mm (système métrique);

ΔL=6,66 mm (système français);

ΔL=4,23 mm (système anglais).

L'augmentation absolue du dessin de base des faces au sens transversal (Δl) s'adopte égale à 75% de l'augmentation du périmètre aux doits (ΔP_d) de l'embauchoir, par le passage d'une pointure à une autre, dans le système particulier de numérotage.

La relation recommandée par la détermination de l'augmentation absolue au sens transversal du dessin de base est le résultat de la nécessité de la transformation dimensionnelle par graduation seulement d'une partie du dessin de base qui couvre la superficie dorsale de l'embauchoir.

Connaissant les dimensions L_0 et l_0 du dessin de base et l'augmentation absolue sur les deux directions étant établies (ΔL et Δl), on peut calculer les augmentations relatives et de toute dimension particulière de longueur et largeur, autre que L_0 et l_0, du dessin de base ou de ses repères au passage d'une pointure à une autre de la série.

Les augmentations relatives et ainsi déterminées serviront à la graduation de toutes les repères de l'ensemble supérieur.

4. Le calcul des augmentations relatives à la graduation des repères de l'ensemble inférieur. Pour la détermination des augmentations relatives et

utilisées à la graduation de l'ensemble inférieur, on considère le contour de la semelle-première correspondant à l'embauchoir pointure N_0, sur lequel on détermine la longueur L_0, mesurée le long de l'axe longitudinale de la semelle-première et la largeur l_0 mesurée perpendiculaire sur la direction de l'axe longitudinale dans la région des doits (zone de largeur maxime).

L'augmentation relative au sens longitudinale (ΔL) sera adoptée égale à l'augmentation de la longueur de la plante de l'embauchoir, par le passage d'une pointure à une autre de la série, distingué selon le système de numérotage (métrique, français, anglais): 5 mm, 6,66 mm, 4,23 mm.

. L'augmentation au sens transversal de la semelle-première s'adopte égale à 1/3 de l'augmentation du périmètre aux doits de l'embauchoir, donc $\Delta l = \Delta l_d$ par le passage d'une pointure à une autre de la série.

À l'aide des pointures $L_0, l_0, \Delta L, \Delta l$, ainsi déterminées, on calculent les augmentations relatives et pour la semelle-première aussi, augmentation utilisées à la graduation de toutes les repères de l'ensemble inférieur.

Dans le Tableau 3 on présente synthétisées les augmentations recommandées à être utilisées à la graduation des repères de l'ensemble supérieur et de l'ensemble inférieur, dans les trois système de numérotage.

Table 3

Le système de numérotage	L'ensemble supérieur		L'ensemble inférieur	
	ΔL	Δl	ΔL	Δl
métrique	5	2,25	5	1,0
français	6,66	3	6,66	1,3
anglais	4,23	1,9	4,23	0,84

Il est possible que pour certains configurations d'embauchoir, notamment pour ceux points, l'augmentation de la longueur et du périmètre aux doits de l'embauchoir, par le passage d'une pointure à une autre de la série, n'avoir pas une dimension constante. C'est pourquoi que nous considérent absolument obligatoire que, antérieurement de l'operation de graduation, se vérifier sur la série des embauchoirs si la variation des dimensions de: longueur, périmètre aux doits et largeur sont des constantes et elles correspondent ou non de point de vue de leur valeur, ceux qui sont précisées dans les tableaux de dimensions des embauchoirs.

Si on signale des déviations des dimensions à la série des embauchoirs, il faut les prendre en considération à la graduation des patrons, pour ne pas arriver dans la situation de où on n'assure pas une correspondance entre les dimensions des repères et l'embauchoir dans le processus de confectionnement des produits. On fait le contrôle de la correction de la graduation par la réalisation de la „série zero".

5. Considérations concernant l'implémentation du programme pour la graduation des repères irréguliers. Les problèmes à résoudre pour la conception et l'implémentation du programme serait [5], [6]:

i) On lit les données d'un fichier créé antérieurement par la collection des données (les coordonnées des points) du contour de la courbe.

ii) Les points peuvent être introduits interactivement et à l'aide du mouse par la visualisation sur le display des coordonnées X et Y de chaque point. Si on désire sauver cette courbe ainsi créée dans un fichier, cela est possible par la sélection de l'option „DESIREZ-VOUS LA SAUVETAGE?" et la mention du nom du fichier où on exécutera la sauvetage.

iii) Après avoir finir d'introduire les données, on appuie sur la taste 1 du mouse (celui de gauche), moment où commence les procedures d'interpolation pour le tracement de la courbe irrégulier [7].

iv) Le programme donne aussi la possibilité d'obtenir une série de pointure d'un repère modelé. Les coefficients de graduation sont calculés selon la méthodologie présentée et sont introduits interactivement, de la tastature, pour obtenir la série de pointure à partir de la pointure moyenne.

v) La réalisation d'une interface soft avec AutoCAD. L'interface est basée sur la lecture de chaque point tracé sur l'écran et son inscription dans un fichier particulier (spécial) de type *.scr qui sera lu par ACAD.

vi) À la fin du déroulement du programme celui qui l'a utilisé est demandé s'il désire la sauvetage du fichier de données et ensuite du fichier de type *.scr. Si on ne désire pas la sauvetage de ces données, le programme sera repris.

vii) À tout moment, le programme peut être interrompu par l'appui simultané des tastes 1+2 du mouse.

6. Conclusions. L'objectif central de l'activité économique déployée dans les sociétés qui produisent des articles de chaussure, dans les conditions concurrentielles de l'économie de marché est constitué par l'obtention de certains produits de qualité aux prix plus bas que possible tant pour les fabricants que pour les bénéficiaires.

Dans le travail on a étudié des possibilités de l'automatisation de quelques phases du processus de préparation de la fabrication, tenant compte des implications majeures que cela démontre dans la réalisation des effets positifs le long de tout le flux de fabrication de la chaussure.

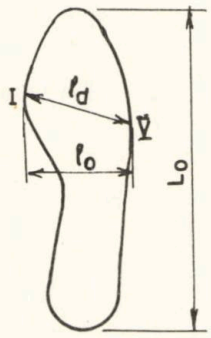

Fig. 4

Fig. 5

On a présenté les principes généraux de variation dimensionnelle des patrons en

série de pointure et, optionnellement, on peut obtenir par le programme la graduation d'un repère en connaissant les coefficients de graduation.

Pour le repère empeigne (Fig.5) on a exemplifié la possibilité du produit soft réalisé concernant la manière d'obtenir la série de pointure.

On apprécie que la méthode élaborée est un premier pas dans la projection assitée par l'ordinateur des produits des chaussures, quoique la réalisation du modèle numérique des repères (donc la phase d'introduction des données) représente une phase un peu difficile, les résultats obtenus sont utiles, avec l'exactitude et la précision correspondantes.

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Chaire de Confections du Cuir

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GRADAREA REPERELOR NEREGULATE

(Rezumat)

In pregătirea fabricaţiei, gradarea reperelor în serii de mărimi constituie o etapă de maximă importanţă, cu implicaţii directe în asigurarea calităţii prelucrărilor tehnologice ulterioare (asamblarea reperelor, formarea spaţială a semifabricatului, executarea de SDV-uri) şi, în final, asupra calităţii produselor.

S-a efectuat un studiu privind gradarea reperelor neregulate şi s-a prezentat un produs soft implementat pe calculator tip IBM-PC ce permite obţinerea seriei de mărimi pentru un tipar al unui produs de încălţăminte.

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L'ÉTUDE DE L'INFLUENCE DES PARAMÈTRES TECHNOLOGIQUES SUR LA QUALITE DES ASSEMBLAGES PAR COLLAGE

PAR
FLORENTINA HARNAGEA et AURA MIHAI

There are presented results of the research of technological parameters that influence the quality of joints by sticking, as: the viscosity of the adhesive solution, the size of the granulation, abrasive paper used at the preparation of the sublayers surface, the drying time of the adhesive film and the time of pressing the joint. By adopting the best values obtained for the resistence of joints by means sticking, the quality of finite products during their utilization is assured.

1. Des considérations théoriques. L'Utilisation dans le processus de la confection des chaussures d'une gamme diversifiée de matériaux synthéques à de différentes propriétés, impose comme une nécessité le choix correspondant des adhésifs, l'application correcte de la technologie d'adhérence, qui conduise à des produits de qualité supérieure, à une bonne résistance de l'assemblage par collage [1].

Genéralement une bonne résistance de l'assemblage par collage qui assure la qualité des finis pendant leur utilisation, on obtient [2], [3] par:

– l'emploi d'un adhésif correspondant pour les matériaux qui s'assemblent;

– la préparation adéquate de la surface des supports destinés à l'adhérance;

– l'appliquation de l'adhésif après la préparation de la surface dans un intervalle correspondant;

– l'emploi de la durée correspondante de séchage de la pellicule adhésive et, éventuellement, avant l'assemblage – activer la pellicule;

– l'emploi d'un temps de pression et d'une pression correspondante.

Concernant les choses mentionnées plus haut dans ce travail, on présente les résultats de la recherche en ce qui concerne l'influence des paramètres technologiques sur la qualité des assemblages par colage. Ainsi, ont été mis en considération les paramètres suivants: la visqueusité de l'adhésif, la grandeur de la granulation du papier abrasif utilisée à la préparation de la surface des supports, le pourcentage d'agent de structuration ajouté dans la solution adhésive, la durée de séchage de la pellicule adhésive et le temps de pression.

2. La partie expérimentale. En vue de la réalisation des expériments on a utilisé des assemblages par colage à des substrats différents: cuir synthétique à support de voile „Pielsin" et caoutchouc durocol. Les éprouvettes employées pour des determination (20×150 mm) ont été prélevés à la longuer du matériel dans le cas du cuir synthétique à support de voile.

Pour l'adhérence des substrats on a utilisé un adhésif à base d'élastomères poliuréthaniques „Aderom 551", avec les caractéristiques suivantes, conformément STAS 11188/92:

– contenu dans la substance sèche: $c=19\pm1\%$;

– visqueusité coupe Ford: temps d'écoulement par ajustage au diamètre de 8 mm, 85±15 secondes.

Le collage des substrats a été réalisée en respectant la technologie classique d'adhérence à savoir:

– la préparation des surfaces des substrats par effilochage avec du papier abrasif, suivi par le brossage des surfaces effilochées;

– le graissage avec de l'adhésif des éprouvettes de cuir synthétique;

– le séchage de la pellicule adhésive, pendant 15–20 minutes;

– activer la pellicule à des températures $T=80$–$90°C$, pendant 10 secondes;

– le collage et la pression des éprouvettes.

L'assemblage des éprouvettes a été faite pour en résulter une sollicitation perpendiculaire sur le plan d'assemblage, en determinant la résistance à la séparation de l'assemblage, la sollicitation à la traction se faisant après 24 heures, 72 heures et 120 heures depuis la réalisation de l'assemblage.

3. Résultats et discussions

a) *La préparation des surfaces des supports* destinées à le collage (cuir synthétique et caoutchouc durocol) a été réalisée par effilochage, en utilisant dans ce sens du papier abrasif de granulation différente. Dans le cas des cuirs synthétiques à support de voile, la préparation consiste à enlever la couche de finissage à l'approchement du support.

L'influence de la grandeur de la granulation du papier abrasif (K) sur la résistance des assemblages par collage dans le cas des expériments employés est présentée graphiquement dans la Fig.1.

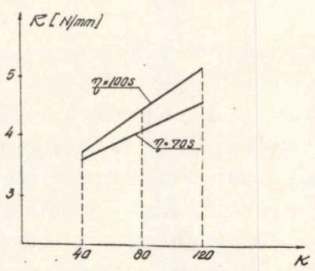

Fig. 1

Bien que la représentation graphique résulte que la résistance de l'assemblage grandit en même temps que la diminution de la granulation de papier abrasif, apparait quand-même l'inconvénient que, de même granulation est plus fine, d'autant plus vite est l'encrassement du papier.

À l'effilochage des surfaces, la profondeur des nérégularités, doit être plus petite que la grosseur optime de la pellicule adhésive (nérégularites pas plus grande de 0,1

mm).

b) *La visqueusité de la solution adhésive* employée doit permettre la pénétration de l'adhésif dans les pores du matériel et un bon chaînage mécanique. La dépendance de la résistance à la séparation de visqueusité de l'adhésif est présentée dans la Fig.2.

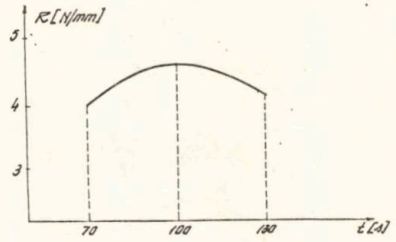

Fig. 2

De la représentation graphique résulte que la valeur optime de la visqueusité conformément STAS 11188/92.

c) *L'Agent de structuration* de type izocianat ajoute dans la solution adhésive au moment de l'utilization en proportion de 10% conduit à l'agrandissement de la résistance de l'assemblage par collage. Les accroissements des pourcentages de la résistance à la séparation déterminée après 24 heures, depuis la réalisation de l'assemblage, sont présentés dans le Tableau 1.

Tableau 1

η	t_p	R [N/mm]		ΔR	
[s]	[s]	0%	10%	[N/mm]	[%]
70	10	2,90	4,00	1,10	38
	30	3,12	4,50	1,38	44
100	10	3,15	4,65	1,40	44
	30	3,41	4,98	1,57	46

d) Après le sédiment de l'adhésif il est nécessaire un temps minimum pour l'évaporation du solvent de la pellicule adhésive liquide.

La dépendance de la résistance initiale mesurée à 5 minutes depuis la pression de l'assemblage, par rapport au temps de séchage, des pellicules adhésives, dans les conditions de l'évaporation du solvent a la température du milieu, est représentée dans la Fig.3.

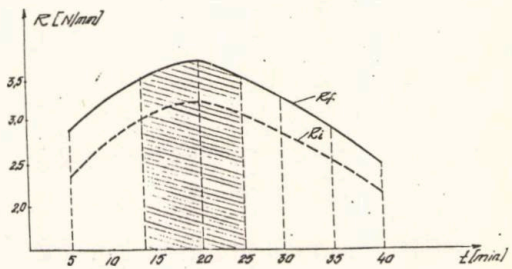

Fig. 3

De la représentation graphique résulte que la durée de séchage de l'adhésif pour lequel la résistance initiale (R_i) et la résistance finale (R_f) de l'assemblage adhésive présentent des valeurs proches de la valeur maximale de la résistance est de 13–15 minutes.

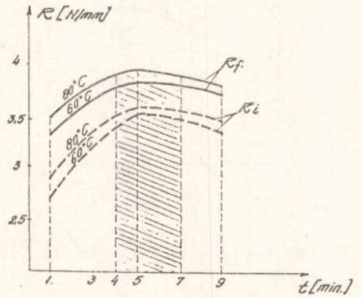

Fig. 4

Le processus d'élimination du solvent de la pellicule adhésive peut être intensifié en employant dans ce sens soit des radiations infrarouges, soit des oudes électromagnétiques [4]. Ainsi, dans le cas du séchage à des radiations infrarouges, après l'appliquation du deuxième support d'adhésif, a résulté un temps optime de séchage sous le fluxe de radiations de 5 minutes, Fig.4.

Dans ce cas de la représentation graphique de la variation de la résistance initiale et finale en fonction du temps d'exposition sous le fluxe de radiations infrarouges on peut déduire la durée de séchage correspondante à l'exposition sous le fluxe de radiations infrarouges des pellicules adhésives; cette durée varie entre 4 et 7 minutes.

e) La résistance de l'assemblage par collage est dépendante à des paramètres auxquels on réalise la pression des substrats combines: temps et pression.

Les assemblages par collage effectués avec le temps de pression compris entre 10–30 secondes, mettent en évidence un léger accroissement de la résistance de l'assemblage en même temps avec l'accroissement du temps de pression, Fig.5.

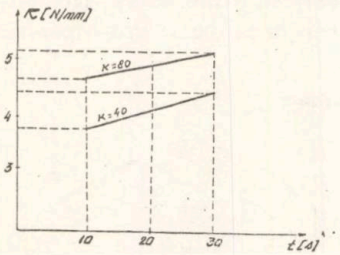

Fig. 5

f) Après la formation de la pellicule solide, dans la pellicule apparaissent des tensions à la suite de sa contraction à la suite de l'élimination du solvent. Ces tensions se réalisent en temps, par la capacité des polimères de relâche des tâches.

Après la réalisation de l'assemblage par collage, on conclut qu'un assemblage ne présente pas maximum de résistance.

Dans le cas de l'adhésion du cuir synthétique avec du caoutchouc durocol, la dépendance de la résistance de l'assemblage en function du temps de pression de l'assemblage jusqu'à la séparation de l'assemblage (du temps de repos), est présentée dans la Fig.6.

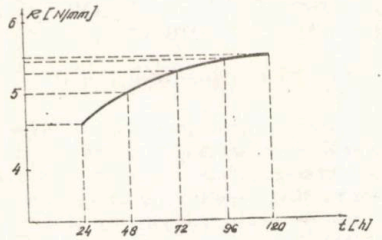

Fig. 6

En résulte donc, un accroissement plus prononcé de la résistance (de 14%) dans l'intervalle de temps 24-72 heures; on considère que le temps de repos de 72 heures est suffisant pour la maturation de la pellicule adhésive.

4. Conclusions

a) Par l'adoption des valeur optimales des paramètres de la technologie etudiés on assure le résistance aux l'assemblage par collage avec un adhésif poliurétanique dans les cas des supports de cuir synthétique et de caoutchouc durocol, résistance réfléchie dans la qualité des produits finis.

b) Parmi les paramètres de la technologie, étudiés, le pourcentage d'agent de structuration ajouté à la solution d'adhesif poliurétanique, présente la plus grande influence sur la résistance de l'assemblage adhésive (on met en évidence des accroissements de la résistance de 38–46%).

c) La réduction du temps de séchage de la pellicule adhésive, par l'intensité du processus de séchage avec des radiations infrarouge, contribue à la diminution du temps nécéssaire pour la réalisation du produit fini, respectivement à l'accroissement de la productivité du travail.

d) La connaissance des paramètres mentionnés offre la possibilité d'intervenir dans le processus de fabrication pour qu'à la fin, on obtienne des produits de bonne qualité, conformément à des conditions techniques imposées.

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Université Technique „Gh.Asachi", Jassy,
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STUDIUL INFLUENŢEI UNOR PARAMETRI TEHNOLOGICI ASUPRA CALITĂŢII ÎMBINĂRILOR PRIN LIPIRE

(Rezumat)

Se prezintă rezultatele cercetării unor parametri tehnologici care influenţează calitatea îmbinărilor prin lipire, cum ar fi. viscozitatea soluţiei adezive, procentul de agent de structurare adăugat în soluţia adezivă; mărimea granulaţiei hârtiei abrazive utilizate la pregătirea suprafeţelor suporturilor, timpul de uscare a peliculei adezive şi timpul de presare a îmbinărilor. Prin adoptarea valorilor optime obţinute pentru rezistenţa îmbinărilor prin lipire se asigură calitatea produselor finite în timpul utilizării acestora.

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Tomul XLII (XLVI), Fasc. 1–2, 1996
Secţia VIII
TEXTILE. PIELĂRIE

SPECIAL FINISHING TECHNOLOGIES FOR THE MODIFICATION OF THE SURFACE PROPERTIES OF THE POLYESTER FIBERS

BY
ROMEN BUTNARU, NICULINA VRÎNCEANU and ANDREI BERTEA

There have been performed treatments for the improvement of the superficial properties of the polyester fibers, using the controlled alkalization technique and plasma treatments. The results show that the maximum modifications of the surface of the polyester fibers are obtained when 400 g/l NaOH and 2 g/l additive are used for the alkaline treatment. A study of the influence of the duration of the treatment in the plasma medium on the intensity of the modifications of the polymer surface is accomplished.

1. Introduction. The improvement of the properties of the polyester textile materials is a very actual issue, considering the high extent of those fibers in the Romanian textile industry and in the international textile industry as well.

There are many possibilities to modify the surface properties of such materials, but from a practical point of view only two are important: the change of the classical finishing technology by introducing new processes and the use of unconventional finishing techniques, such as controlled alkalization or plasma treatment.

The present paper is showing comparatively the modification of the surface proprieties of a polyester fabric that was treated with alkaline substances and with cold plasma.

2. Experiments. The treated material was a cotton/polyester blend, with a 100% cotton warp and a 100% polyester weft. The polyester was from four sources, as it can be seen from Table 1.

Table 1
Physical, Chemical and Structure Characteristics of the Polyester Fibers that Have Been Studied

Nr.	Characteristics	Polyester type			
		A – Jassy	B – C.M.	C – Corabia	D – Taiwan
1	Contraction at boiling, [%]	2.5...3.3	4.1...4.7	5.0...7.3	1.7
2	Contraction in hot air (210°C), [%]	10.4... ...11.2	11.5... ...16.2	14.5... ...17.9	10.5
3	Iodine absorbtion, [mg I_2/g fiber]	102...135	106...141	116...150	102
4	Critical dissolving time, [sec.]	3...6	3...5	2...4	10
5	Birefringence	0.185...0.219	0.203...0.221	0.200...0.209	0.192
6	Degree of cristallinity, [%]	34.3...38.7	28.7...35 2	27.9...31.4	38.4
7	Oligomer content, [%]	1.6...1.8	1.7...2.2	1.9...2.2	1.58

For the same samples there have been made two series of experiments, one with alkaline treatment, the other with plasma treatment.

The alkaline treatment comprises the following steps: a) impregnation and squeezing on a foulard in four variants of NaOH and additive (ethyl pyridine bromide) concentration (Table 2); b) 90 seconds vaporization at 100°C; c) very hot washing, then warm and cold washing; d) neutralization and a new washing.

Table 2

Parameters of the Alkaline Treatment

Nr.	Variant of treatment	Parameters of the alkaline treatment	
		NaOH concentration, g/l	Additive concentration, g/l
1.	Blank sample – M	0	0
2.	Variant 1 – R_1	400	0
3.	Variant 2 – R_2	300	2
4.	Variant 3 – R_3	400	1
5.	Variant 4 – R_4	400	2

The effects that were obtained on surface properties were evaluated by determining the weight losses and the hydrophilic properties (Table 3).

Analyzing data from Table 3 one can see that for every type of polyester that was tested the use of the additive leads to an intensification of the alkaline hydrolyses, respectively at higher weight losses. The increase of the weight loss is directly proportional with the increase of the NaOH and additive concentration. The same is the variation of the hydrophilic properties.

In what concerns the influence of the polyester type, it can be seen that in the same condition bigger losses are present at polyester type C (Fig.1). This type of polyester shows the bigger hydrophily modification as well. This can be explained analyzing the supramolecular structure of the polyester samples. Polyester type C has the biggest iodine value, the lowest critical dissolution time, which means that its structure is less crystalline and not very ordered.

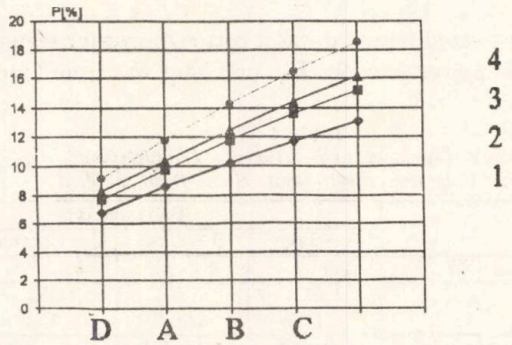

Fig. 1.– Weight loss of the textile material depending of the type of treatment and the type of the polyester: *1* – R_1 variant; *2* – R_2 variant; *3* – R_3 variant; *4* – R_4 variant.

Because it is considered that the optimum superficial properties are obtained at a weight loss of 15% [1], it results that the best variant is the treatment with 400 g/l polyester and 2 g/l additive, applied on polyester type C.

Table 3

Results of the Experiments Performed in Alkaline Conditions

Nr.	Composition	Variant	Loss of weigh in the weft, [%]	Hydrophilic properties	
				Water uptake by diffusion, [%]	Absorption time, [sec]
1.	Warp: 100%	M	–	148	85
	cotton	R_1	8.6	160	2
	Weft: 100%	R_2	9.8	168	0
	polyester	R_3	10.4	176	0
	type A	R_4	11.8	179	0
2.	Warp: 100%	M	–	154	64
	cotton	R_1	10.2	164	1
	Weft: 100%	R_2	11.8	173	0
	polyester	R_3	12.5	179	0
	type B	R_4	14.3	184	0
3.	Warp: 100%	M	–	158	41
	cotton	R_1	11.7	167	0
	Weft: 100%	R_2	13.6	169	0
	polyester	R_3	14.4	181	0
	type C	R_4	16.5	186	0
4.	Warp: 100%	M	–	140	99
	cotton	R_1	6.8	153	3
	Weft: 100%	R_2	7.7	160	0
	polyester	R_3	8.3	169	0
	type D	R_4	9.2	171	0

The same types of polyester materials have been treated in plasma medium. The treatment conditions are the following [2]: a) treatment medium: air; b) pressure: 1 tore; c) power of the installation: 1 kW; d) treatment time: 10-600 seconds.

Table 4

Results of the Cold Plasma Treatment of the Samples

Nr.	Composition	Treatment time, sec	Diffusion uptake, %	Speed of the diffusion, [cm/min]			Absorption time, sec
				0.5'	3'	10'	
1.	Warp: 100%	0	148	9.0	18.2	20.0	85
	cotton	10	166	27.5	34.0	34.2	6
	Weft: 100%	300	171	33.7	35.5	36.5	1
	polyester A	600	172	34.0	35.5	36.5	0
2.	Warp: 100%	0	154	9.0	22.7	25.0	64
	cotton	10	169	28.5	34.2	34.2	5
	Weft: 100%	300	172	34.0	35.5	36.3	0
	polyester B	600	174	34.5	35.5	36.7	0
3.	Warp: 100%	0	158	10.0	22.9	27.5	41
	cotton	10	170	32.0	38.0	38.7	2
	Weft: 100%	300	173	38.2	38.7	33.7	0
	polyester C	600	175	39.5	40.0	40.0	0
4.	Warp: 100%	0	140	8.0	17.0	18.5	99
	cotton	10	160	32.2	34.7	35.7	8
	Weft: 100%	300	170	33.7	35.7	36.0	0
	polyester D	600	171	35.7	37.0	37.0	0

For the treated samples it has been determined the diffusion moisture uptake, the speed of the diffusion and the absorbtion time. Results are shown in Table 4.

The analysis of this data leads to the following conclusion: the plasma treatment improves significantly the hydrophilic properties, whatever the type of polyester is.

Important increases in the hydrophilic characteristics of the material occur at a plasma treatment of 10 seconds. When increasing the duration of the treatment, the effect is the same, and this means that plasma treatments of more than 10 seconds are not justified [3].

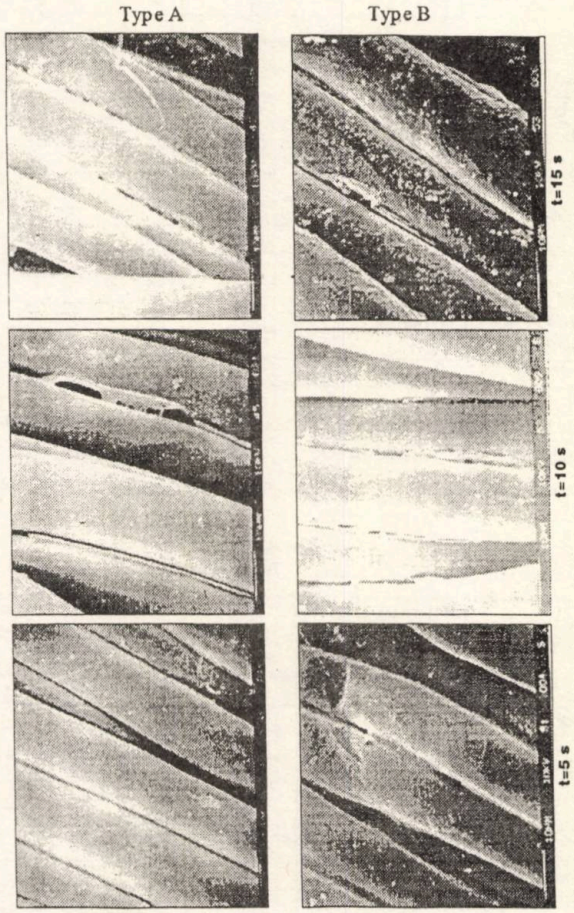

Fig. 2.– *a*) Photographic images (electron microscopy) of the surface of the polyester fibers from different sources treated with plasma at a duration of 5, 10 and 15 seconds.

The effect of increasing hydrophily after the plasma treatment can be explained by the structural modification that takes place (the disorder of the macromolecular chains) and the morphological changes suffered by the fibers. This phenomenon are

confirmed by electron microscopy (Fig.2).

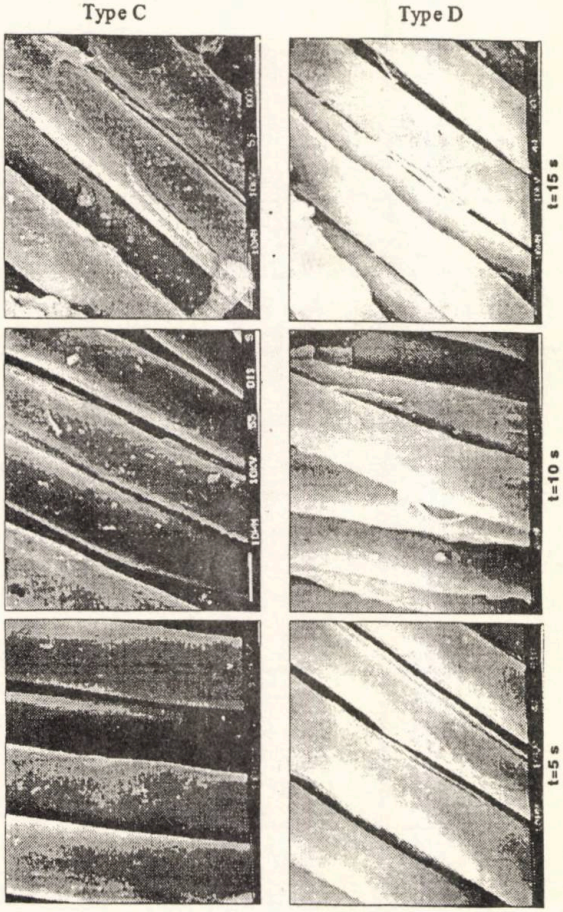

Fig. 2.– *b*) Photographic images (electron microscopy) of the surface of the polyester fibers from different sources treated with plasma at a duration of 5, 10 and 15 seconds.

The IR spectrums for the plasma treated and untreated samples of polyester type C (Fig.3) show the appearance of some changes in the 3500 cm^{-1} wavenumber zone, which is characteristic to the hydroxyl group, the one that is responsible for hydrophily. The height of the peak corresponding to this wavenumber increases with the duration of the treatment in the interval 0-10 seconds. Comparing the spectrums for the four types of polyester (Fig.4), all treated for 10 seconds with cold plasma, it can be seen that the height of the peak for the 3500 cm^{-1}, as well as the hydrophilic properties, increase in the order: D<A<B<C. This is the order the crystallinity of the polyester types decreases.

Comparing the results for the alkaline treatment and the cold plasma treatment

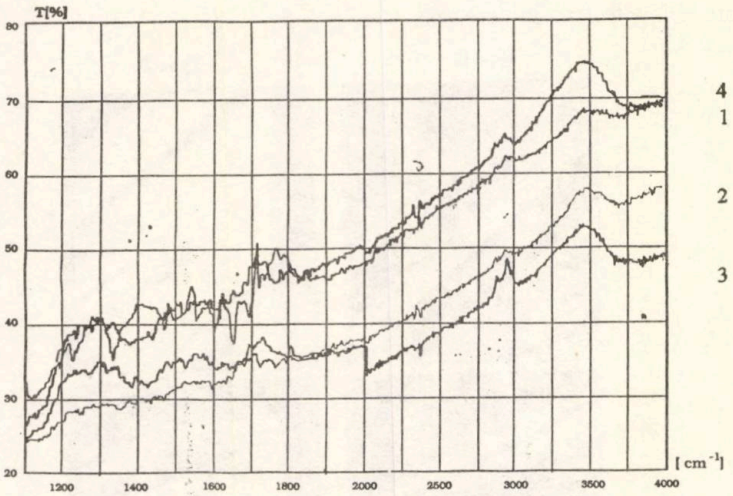

Fig. 3.– IR spectrum of the type C polyester treated with plasma al different duration: *1* – untreated; *2* – 5 seconds; *3* – 10 seconds; *4* – 15 seconds.

concerning the hydrophilic properties, it can be seen that the same effect with that of a 15 seconds plasma treatment is obtained if the sample is treated in alkaline condition (variant R_2), that means 300 g/l NaOH and 2 g/l additive.

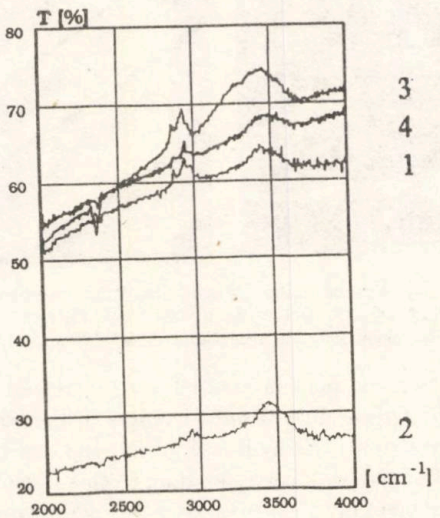

Fig. 4.– Details of the IR spectrum (range 2000-4000 cm^{-1}) for polyester from different sources: *1* – polyester type A; *2* – polyester type B; *3* – polyester type C; *4* – polyester type D.

3. Conclusions. a) There have been performed treatments for the improvement of the superficial properties of the polyester fibers, using the controlled alkalization

technique and plasma treatments.

b) We found that the maximum modifications of the surface of the polyester fibers is obtained when a 400 g/l NaOH and 2 g/l additive is used for the alkaline treatment.

c) The duration of the treatment in the plasma medium that provides best superficial properties of the polyester fibers is of approximately 10 seconds.

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TEHNOLOGII SPECIALE DE FINISARE PENTRU MODIFICAREA PROPRIETĂŢILOR DE SUPRAFAŢĂ ALE FIBRELOR CELULOZICE

(Rezumat)

Se urmăreşte comparativ eficienţa tratamentelor alcaline şi cu plasmă rece în vederea modificării caracteristicilor de hidrofilie ale fibrelor poliesterice. Efectele modificării proprietăţilor superficiale s-au apreciat prin determinarea pierderilor de masă şi a hidrofiliei, constatându-se eficienţa similară a tratamentului alcalin cu 300 g/l hidroxid de sodiu şi 2 g/l aditiv şi a tratamentului cu plasmă timp de 10-15 secunde.

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Secţia VIII
TEXTILE. PIELĂRIE

STUDIES CONCERNING THE TANNING OF HIDES WITH CHROMIUM BASIC SALTS IN THE PRESENCE OF SOME ANIONIC POLYELECTROLYTES

BY

DOINA-IRIDENTA COSTAŞ, GABRIELLE-CHARLOTTE CHIŢANU, ADRIAN CARPOV, N. BADEA, DOINA CREANGĂ, AL. MĂLEANU, LĂCRĂMIOARA-IRINA ZAHARIA, OLGA SAUCIUC and SERGIU SAUCIUC

This paper presents a review of the problems and difficulties appeared in the tannage of hides with chromium basic salts especially the waste water treatment and of the literature data concerning this topic.

There are also presented some own results about the use of maleic acid polyelectrolytes in the chrome-tanning of cattle hides. Two aims were attained: the decreasing of the chromium salt offer and the minimizing of the Cr_2O_3 content in waste waters.

1. Introduction. The leather industry is permanently confronted with new problems due to the requirements concerning the discharge of waste waters and the removing of sludges.

One of the components mostly incriminated in waste waters is chromium, as CrIII. The presence of CrIII is not allowed neither in discharged effluent (the maximum permitted concentration is 1 mg/L [1]), nor in the sludge, because disfavors its agricultural use. Regarding to the use as a water resource for irrigation, there are limits imposed concerning the toxic or harmful indicators, among which the chromium content is mentioned [2].

Despite to the relative weak toxicity of CrIII, the control of the effluent and sludge discharge is becoming more strict in the whole world, as a precaution concerning the theoretical possibility of its oxidation to CrVI. In countries in which the environmental legislation is more advanced, the removal of solid wastes and sludges is not permitted because of the organic substance contents and, last but not least, of the chromium contents [3].

Waste waters from tanning of the cattlehides have the concentration between 4-10 g Cr_2O_3/L comparing to the offer of 1,8-2,2% Cr_2O_3 over the hides, this loss ranging among the limits of 15-30%. In Romania, to the quantity of raw hides processed in 1991, the loss through waste waters from the tanning was about 250 tones Cr_2O_3, 500 tones sodium bichromate, respectively [4].

The nowadays orientation concerning the chromium basic salts is that they must not leave from tanning system, but in very small quantities, either recovered from waste waters, sludges, solid waste ashes, or directly recirculated as solution [5].

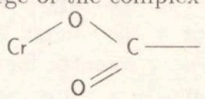
Undoubtedly, the recovery of chromium basic salts represents a practical and economical way to minimize the chromium loss. The problem of pollution produced by chrome-tanning of hides can be reconsidered if the tanning technological orocess is improved using some "ecological" materials which reduce the quantity of chromium basic salts both for tanning and from waste waters.

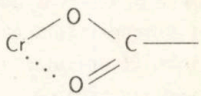
2. General Outlines. The main priority in the leather industry is to provide high quality products assuring a good environmental protection. Problems as: lowering of chromium content in waste waters or solid wastes, organic pollution, high water consumption, solvent use are still waiting for an answer. To solve these problems, for example, in the IVth Framework Programme of European Union is included a special programme concerning the Environment and Climate for the period 1994-1998 [6].

The improvemnt of tanning technologies to an ideal process is an alternative recommended more and more often in the literature. The chrome-tanning process requires the diffusion in hide in equilibrium with the combination by chemical reaction. The general principle of all methods for improvement of technologies is the creation of conditions for a rapid reach of equilibrium which determine the increase of the binded chromium quantity.

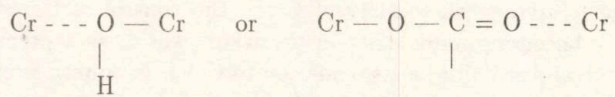
One of the modern trends concerning the increase of the efficiency of chrome-tanning is the use of complexing agents which change the affinity of complexes for the hide, inducing a better binding of chromium.

Dicarboxylic organic acids are among the complexants able to improve the chromium fixation in hide and to produce a better liquor exhaustion. The undissociated carboxylic group can form coordinative bonds by one or both oxygen atoms without changing the charge of the complex ion. In its turn, the dissociated carboxylic group can form a covalent bond with chromium or a covalent bond and a coordinative one, modifying the charge of the complex ion.





In polynuclear complexes, –OH and –COOH groups can form bonds of the type:



It is supposed that, at low pH values, dicarboxylic acids enter in the inside sphere of the chromium complex with –COOH undissociated groups, and at high pH values, with the dissociated –COOH groups.

The study of the influence of dicarboxylic acids on the masking effect of the chromium basic salts by UV-VIS spectrophotometric method, leads to the conclusion that, generally, the masking effect decreases with the increase of the number of carbon atoms in the molecule of the aliphatic dicarboxylic acid. Also, once reaching the collagen matrix, the chromium salts masked with dicarboxylic acids participate at a series of reactions with the reactive groups of the polypeptidic chain. At the pH of chromium liquors, basic or weak acid groups (–COOH, $-NH_2$, –OH), displace

the carboxylic groups of acids from the masked chromium complex. Therefore a chromium transfer in hide takes place. The dicarboxylic acids partially elliberated can resume this cycle of chromium transfer in hide.

In the case of split gelatin and thin hides this tanning method with dicarboxylic acids doesn't raise problems, more complicated being the tanning of the unsplit gelatin hides. To solve this problem, for some years, some anionic polyelectrolytes are starting to be used.

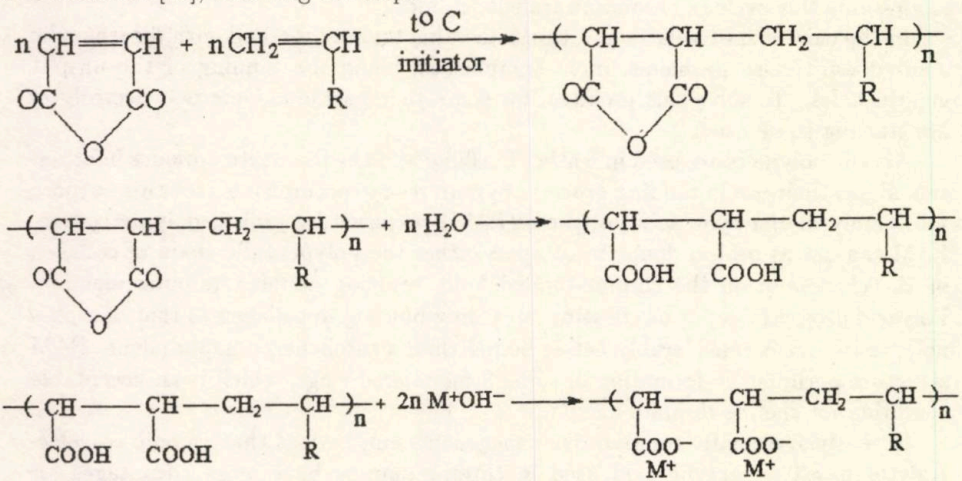
Acrylic polymers are used in leather finishing and the literature provides information about their use in tanning process. Syntan resins recommended for this purpose are mainly methacrylic acid polymers (PAM) prepared by radical polymerization. PAM can act as proton donor to complex either the polypeptidic chain of collagen or the chromium on the chrome-tanned hide, bringing about a tanning reaction. Polyacid geometry is not as effective in causing binding to collagen as that of a phenolic resin, but is considerably better bound than a sulphonated naphthalene. PAM structure permits the formation of some 8 membered rings, which is an acceptable condition for chelate formation.

Recently systematic comparative experiments emphasized that anionic polyelectrolytes based on acrylic acid used in chrome-tanning have more advantages for increasing the chromium fixation (BASF, 1990). The most important parameters to optimize the chromium fixation and formulations suitable to practical use have been established [10]. The polymer treated leather has a dense face and fine pores. The option between the use of dicarboxylic acids and polymers with acid groups is made depending on the specific features which are desired.

A very recent investigation (1993) made by specialists from Cromogenia Units S.A Spain followed up the influence of polymer use in tanning process on the physicochemical and dyeing properties of the tanned hides. The products used, from Retanal series, are copolymers of maleic acid, poly(acrylic acid) as sodium or ammonium salts, condensation products of melamine with dicyandiamide and/or lignin derivatives, phenol-formaldehyde resins. The results obtained also showed the influence of polymer chemical structure on the quality and features of the tanned hides. For example, the use of the maleic acid-styrene copolymer is adequate for the obtaining of dense-face and fine-pore leathers for either clothes and footwear manufacture. From the point of vue of the specialists in polyelectrolyte chemistry, the use of some maleic acid copolymers for hide chromium fixation, seems to us to be favoured by the presence of the two adjacent carboxylic groups from the maleic acid units. It is well-known the increased capacity of binding of some divalent ions at maleic acid copolymers [12], which lies at the basis of some practical uses of these copolymers in detergent industry or as scale and corrosion inhibitors. In literature is also cited the formation of complexes between maleic acid copolymers or other anionic polyelectrolytes and peptides or proteins.

3. Results and Discusions. In this paper are presented the results obtained for the use of some dicarboxylic polyelectrolytes in hide tanning with chromium basic salts. Such polyelectrolytes are obtained by the copolymerization of maleic anhydride with vinylic comonomers, followed by the hydrolysis of anhydride rings

and the neutralisation of carboxylic groups thus obtained with inorganic hydroxydes or carbonates [15], following the steps:



As it can be seen the position of the carboxylic groups encourages the polyvalent ions binding. Moreover, the products from this class are non-toxic and can be named as "ecologically friendly". This fact was demonstrated by the tests made between 1986-1988 by the Institute of Hygiene and Public Health, Jassy Branch, Romania, which classified these products in the "4th toxicity class, practically non-toxic products".

The use of these polyelectrolytes in tanning is made in the most simple way, by direct dosing during the tanning operation. Industrial tanning experiments made with dicarboxylic polyelectrolytes showed that it is possible the lowering of chromium basic salts offer of about 0.3-0.4% Cr_2O_3 compared to the usual offer of 2.0% Cr_2O_3. The Cr_2O_3 content in waste liquor has also drastically decreased, up to 0.2-1 g Cr_2O_3/L. The leather thus obtained have the physico-chemical properties inside the limits of Romanian State Standards (STAS):

Table 1

Parameter	MU	Sample		STAS 1659/19
		1	2	
Thickness	mm	2.0	1.9	
Breaking strength	N/mm^2	27.1	48.6	min. 20
Elongation at effort of 10 N/mm^2	%	26	26	12–28
Tearing strength	N/mm^2	25	45	min. 30
Contraction index	%	0	0	max. 5
Humidity	%	10	9.9	10-15
Cr_2O_3	%	4.6	5.7	min. 3.5
Total ash	%	5.05	6.1	max. 2.5 over % Cr_2O_3

4. Conclusions. a) The progressis in leather industry and the constraints of Environmental Legislation have imposed to the scientists working in this domain to find new answers. One of the recent solutions proposed is the use of polymers to

reduce the chromium offer and to lower the Cr_2O_3 content in waste waters.

b) The preliminary results from this paper emphasized the promissing issues for the use of dicarboxylic polyelectrolytes containing maleic acid, whose structure allows a better fixation of chromium in hide. The qualities of the tanned leather are similar to those tanned by classical methods. In the same time the waste waters have a very low content of Cr_2O_3.

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STUDII PRIVIND TĂBĂCIREA PIEILOR CU SĂRURI BAZICE DE CROM ÎN PREZENŢA UNOR POLIELECTROLIŢI ANIONICI

(Rezumat)

Se face o trecere în revistă a problemelor şi dificultăţilor care apar în procesul de tăbăcire cu săruri de crom, în special tratarea apelor uzate rezultate şi a datelor de literatură privind acest domeniu.

Sunt prezentate, de asemenea, rezultatele proprii privind utilizarea unor polielectroliţi anionici dicarboxilici la tăbăcirea cu săruri de crom a pieilor de bovine, având ca scop reducerea ofertei de

săruri de crom concomitent cu micşorarea conţinutului de Cr_2O_3 în apele reziduale.

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Secţia VIII
TEXTILE. PIELĂRIE

APPLICATION OF "MACTOR" METHOD ON THE ACTIVITIES OF THE MAINTENANCE FIRMS IN THE CONDITIONS OF THE ACTUAL TRANSITION PERIOD TOWARDS THE COMPETITIVE ECONOMY

BY

I. VERZEA and COSTACHE RUSU

For the elaboration of a strategic plan, a maintenance firm must know the rapport of forces with the opponents. In this paper we are solving the problem, proposing an extension of the MACTOR method.

1. Introduction. The present paper proposes an extension of the MACTOR method on the activity of a maintenance firm, in the context of the actual socio-economic background in Romania.

The method proposes to solve the problem in finding out the rapport of forces between the firm and the opponents in the view of establishing the premises for the elaboration of a strategic plan. It was first used in 1970 by Paris Airport, France. The working method, as well as the result that was obtained, constituted a secret for 20 years, period for which the strategy had been elaborated.

The extension of the field possible due to the similitude existing between a transport activity and a maintenance one: close relationships with business partners, strong competition in the field, the possibility of being influenced by opponents, by one or more intermediary and common factors of pressure.

2. Stages of MACTOR Method. The method proposes the passing of the steps presented in Fig.1. Afterwards, we will approach each stage separately, by applying them to the activity of the maintenance firm, named in our paper M.

3. Presentation of "actors". Any firm or institution has its purpose to obtain advantages to the mission and the established objectives. Approaching this problem in this context, "the actors" that interfere in this strategic game are the following: the maintenance firm M, the State and the firm assisted by the maintenance firm.

Since the name of the method comes from "the *matrix* of the *actors*", the notion "actor" will be used, having the meaning of business partner or opponent. The problems, objectives as well as the activities undertaken by actors in their confrontation on the market are schematized in Table 1.

In the table is illustrated the relation established between the actors through the actions undertaken in relation to the opponents. On the diagonal there have been emphasized the objectives and the specific problems of each actor.

In fact, the problem is much more complex. For instance, the State may be

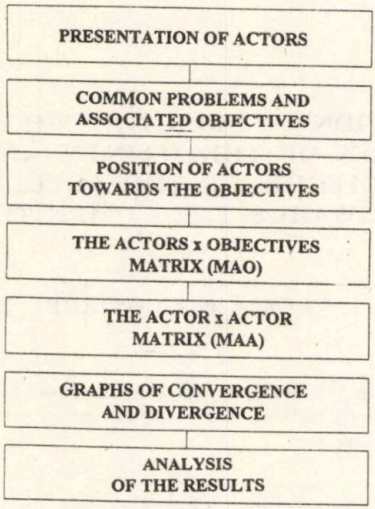

Fig. 1.– Stages of the MACTOR method.

represented by financial institutions or by legislative power and the assisted firm could be one involved in any field and have the liberty to appeal to any competitor firm to M. Each actor can act on the others either directly, or through the agency of one or more intermediary, through specific levers. The problem may become complicated the moment when we want to overtake the whole complexity. For this reason we will emphasize only some actors $A_i, i = 1,5$, considered as *most important* in this problem: A_1 – the maintenance firm M; A_2 – the firm assisted by firm M; A_3 – the ecological organizations; A_4 – the Romanian State; A_5 – the competitor firms.

4. Common Problems and Associated Objectives, Specific to the Actual Transition Period to the Competitive Economy. Considering the entire complexity of the problem, we extract the important problems, common to more actors. These are:

– lack of financial funds;

– variety and complexity of tools;

– lack of support of the productive and maintenance activities and research from the State;

– admissible norms for the pollution of the environment incompatible with the actual technical and technological level;

– the national economic crisis.

To these problems we will associate specific objectives O_j, in comparison to which each actor will specify its position: O_1 – straightening of the position on the market of the maintenance activity; O_2 – straightening of the position of the assisted firm on the market of productive activities; O_3 – increase of the technical and technological

level; O_4 – standardization of technical and constructive characteristics of the tools; O_5 – application of international standards in the environment pollution control; to avoid complications of the problem.

Table 1
Presentation of Actors

Actors towards actions	The assisted firm	Maintenance firm M	The State
The assisted firm	**Objective**: Survival ad avoidance of crisis **Problems**: – low demand of products; – imposed limits to admissible pollution; – low technical level; – lack of capital; – lack of support of production and innovation from the State.	**Actions**: – imposition as short as possible schedules for faults remedy; – imposition of quality standards the activity performed by the maintenance firm; – penalization in the case of non-observance of the above conditions terms.	**Actions**: – demonstrations, strikes, lobby actions in order to obtain rights and facilities in the development of productive and research activities; – frequent demands of exemption from taxes and for benefices, imports and exports.
The maintenance firm M	**Actions**: – specific activities of maintenance and repairs; – pressing to increase the terms of the activities achievement; – request of supplementary funds mecessary in solving unexpended problems occurred performing services.	**Objective**: Economic growth and crisis avoidance **Problems**: – low demand in services; – performance limits imposed by the beneficiary; – outdated technical equipment; – imposed execution terms; – the variety of industrial tools.	**Actions**: – pressure in obtaining funds for development and research and for encouraging a policy or reconsideration of the role that the maintenance activity in the strategy of national development.
The State	**Actions**: – control of activity through majority in representation and property; – imposing taxes level trough financial levers; – encouraging the activities according to governing program; – imposing the admissible norms for consumption and pollution.	**Actions**: – control of activity through majority in representation and property; – imposing taxes level through financial levers; – encouraging the activities according to governing program; – imposing of admissible norms for consumption and pollution.	**Objective**: Increase in competitiveness of the economic activities in the world **Problems**: – lack of credibility in the world; – the actual world socio-economic conjuncture; – lack of credibility of State institutions on the national plan.

5. Position of the Actors to the Objectives. In comparison with the objectives, each actor can have a divergence or a convergence. The numbers of actors and

established objectives are not supposed to be excessive **in order** relation, depending on interest. These relations best suit to a graph representation, by associating the "+" sign with a convergence relation and the "−" sign to a divergent one, according to the model showed in the Fig.2.

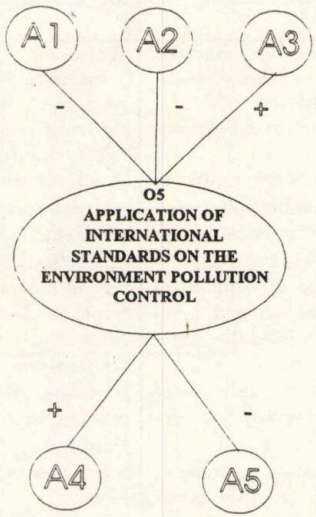

Fig. 2.– Graph of the actors' position towards the objective O_5.

For each objective such a graph can be drawn out, but for space reason only the graph associated with the objective O_5 is *illustrated.*

6. The Objectives × Actors Matrix (MAO). In order to allow hierarchical position of each actor in relation to each objective, we are applying ranks from -3 to $+3$ as follows:

$-/+3$, if the actor's divergence/convergence towards the objective is strong;

$-/+2$, if the actor's divergence/convergence towards the objective is of medium intensity;

$-/+3$, if the actor's divergence/convergence towards the objective is weak;

0, if the actor is indifferent to the objective.

The point of departure is the graph of the actor's position towards the objectives. Consequently, the matrix shown in Table 2, named MAO, is obtained.

A general view of this matrix cold leads us to some conclusions, as:

– some actors manifest multiple convergence with the objectives (ex. A_3);

– some objectives are in the attention of more actors while others have connections with some of them (ex. O_1);

– some actors manifest divergence with the objectives (ex. A_5).

7. The Actors × Actors Matrix (MAA). Having the position of the actors towards the objectives established (see last chapter), our purpose is to establish the

Table 2
MAO Matrix

Actor A_i	A_i/O_j	O_1	O_2	O_3	O_4	O_5
The maintenance Firm M	A_1	3	3	2	−1	−2
The assisted firm	A_2	0	0	2	−1	−2
Ecological organizations	A_3	0	0	1	2	3
The State	A_4	0	−3	0	0	3
Competitor firms to M	A_5	−3	3	−2	−1	−2

number of convergence and divergence between each couple of actors. The working method is relatively simple, multiplying the MAO matrix with its transposing matrix (which becomes MOA, objectives×actor matrix), differentiating the positive values from the negative ones obtained, as in Table 3.

Table 3
MAA Matrix

Actor A_i	A_i/A_i	A_1	A_2	A_3	A_4	A_5
The maintenance Firm M	A_1	–	9 −8	2 −8	0 −15	14 −13
The assisted firm	A_2	9 0	–	2 −8	0 −6	5 −4
Ecological organizations	A_3	2 −8	2 −8	–	9 0	0 −10
The State	A_4	0 −15	0 −6	9 0	–	0 −15
Competitor firms to M	A_5	14 −13	5 −4	0 −10	0 −15	–

The values obtained in the matrix will constitute the base in the elaboration of the conclusion and will constitute, for a complete characterization of the force's rapport, the point of departure in drawing out complete convergence and divergence graphs.

The values obtained in the matrix will constitute the base in the elaboration of the conclusion and will constitute, for a complete characterization of the force's rapport, the point of departure.

8. Complete Convergence and Divergence Graphs. The position obtained in the MAA matrix points out the convergence between the actors towards objectives, the negative ones expressing the divergence. For a better illustration of these aspects as well as the links established between the actors, we resort their representation in convergence and divergence graphs, as it results from Figs.3 and 4.

9. Interpretation of the Results. The analysis of the results shows us the joins favorable to the objectives. We remark the direct convergence in approaching the objectives between the actor A_1 and the actors A_2, A_3 and A_5, while the State (A_4) is convergent to the firm M indirectly. The divergent connections result from the graph of Fig.4, observing that A_1 (M) is directly divergent to A_3, A_4 and A_5 and indirectly to A_2 (the assisted firm).

Analyzing the values obtained in the matrix MAA, we can draw conclusions regarding the position of firm M towards other actors as:

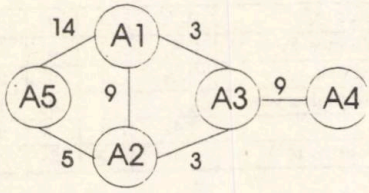

Fig. 3.– Complete convergence graph.

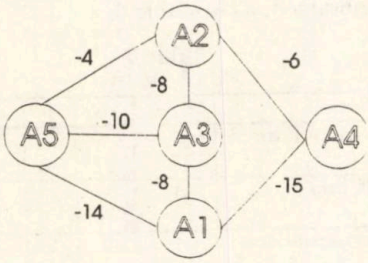

Fig. 4.– Complete divergence graph.

– strong convergence (+9) between the actions of firm M and the assisted firm, reflecting the cooperation between them in the current activity, while the divergence is minimum (0);

– strong divergence towards the ecological organizations (–8), correlated with a low concern to assure the environment protection (+2), attitude which is specific to the actual economic situation;

– the convergence between the firm M and the State is 0, in exchange, the divergence is of great values (–5), clearly illustrating the rapport established: the firm is not supported in the activity development, but through different levers it is strongly restricted;

– strong involvement of the firm M in the struggle with the competitors, expressed both by a high convergence (+14) with the A_5 against ecologist organizations and strong divergence, specific in the market competition.

Analyzing the matrix as a whole, we can also draw conclusions regarding the position of the other actors towards the context, conclusions that can be useful in the perspective elaboration of a strategic plan.

For instance:

– The State keeps extremely strong divergence towards all the economic agents (represented in the model by firm M, assisted firm and competitors), as a result of the actual lack of credibility and excessive fiscality, the only convergence being established with the ecological organizations that it supports;

– The competitor firms are as well in divergence relations with all the actors, more important being those with the firm M and the State. However, convergence

with the firm assisted by the firm M have been recorded. That is the sign that the assisted firm has availability to the cancellation of some contracts with the firm M, with a view to obtain some advantages that the competitor can offer;

– The ecological organizations are in a strong divergence, not only with the firm M, but also with all the economic agents;

– The assisted firm is also in divergence both with the State and the ecological organizations, the strongest convergence being with the firm M, with whom it cooperates, but also with the future potential contractors of the maintenance activities.

10. Conclusions. Conformed with direct and indirect opponents, the maintenance firm has to know in any moment the force's rapport towards the opponents. It is for this purpose that the MACTOR methods applied in the present paper. For each step, there have been coefficients established and used and also there have been estimations of the influence factors resulted from experiments and personal appreciation.

From the analysis of the outcome, it results a close cooperation between the maintenance firm and the assisted firm, based on mutual interest, but also multiple divergence towards the competitors and the State. Quantifying this rapport, there have been substantiated the premises in drawing out a correct strategic plan with real chances of success.

The method still remains a challenge directed to managers. Its applicability could be extended to firms from other activity fields, confronted with specific problems.

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APLICAREA METODEI „MACTOR" ÎN FIRMELE DE MENTENANŢĂ, ÎN ACTUALA PERIOADĂ DE TRANZIŢIE SPRE ECONOMIA CONCURENŢIALĂ

(Rezumat)

Se propune o extindere a domeniului de utilizare a metodei MACTOR, prin aplicarea ei la activitatea unei firme de mentenanţă, în actualul context socio-economic din România.

Metoda propune rezolvarea problemei de identificare a raportului de forţe existent între firmă şi adversari, în vederea constituirii premizelor elaborării unui plan strategic organizaţional.

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